

GENERAL CHEMISTRY

FOR COLLEGES *Fourth Edition*

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P R E F A C E

THIS FOURTH EDITION is based upon the same objectives and follows the same general outline as the previous editions. Many sections and some chapters have been largely rewritten. Some of the chapters have been combined and in others topics have been regrouped. Thus, the former chapter dealing with the laws of chemical change has been combined with the one on Dalton's Atomic Theory. A greater amount of material on the structure of matter has been placed in an early chapter. The material of the later chapters on this subject has been rearranged, rewritten, and supplemented with new material on nuclear chemistry, atomic energy, and related topics.

Among other changes that may be noted are the following: a new chapter on oxidation and reduction, a change in the form of the periodic table on the inside back cover, the numbering of the sections in each chapter, the additions of material on silicones, trace elements, transuranium elements, and other topics of recent interest, new illustrations, the omission of descriptions of the Le Blanc and Arc processes, and changes in the sequence of some of the earlier topics. It is hoped that the double-column format may be convenient and helpful because of the shorter lines and the greater amount of material that is presented on a single page.

This and the previous editions were prepared for use by students in the elementary chemistry course of colleges and universities. The author has considered his readers as students who are studying chemistry for the first time. However, the nature of the material presented is sufficiently different from that of high-school texts and is sufficiently complete to serve as a textbook for students who have had an introduction to the subject before entering college.

Three major objectives of the elementary chemistry course have determined the nature of the subject matter and the order of presentation. (1) The author believes that the student should obtain, first of all, appreciation and understanding of how the science that he is to study has grown into what it is today. This means that he must be led to see how facts have been collected and how they have been interpreted in deriving basic principles and in formulating theories. Step by step, the student must follow the scientific reasoning of the eighteenth and nineteenth centuries until the kinetic theory, the atomic and molecular hypotheses, and the nature of chemical change become natural and logical conclusions of his own. (2) As soon as possible, the student should be made aware of the vast store of information concerning the structure of matter and the nature of the physical world that has been made available to students of science by twentieth-century investigations of the atom and the molecule. This material should be used, wherever possible, in the interpretation of chemical behavior and chemical changes. (3) After the establishment of the basic

frame work of the science and the development, on his part, of an ability to reason in terms of chemical principles, the student should be encouraged to use this knowledge to reason intelligently about the nature of the world in which he lives, about himself, and about the many products that nature and industry provide for his needs and comfort.

The opening chapters tell the story of the establishment of the fundamental laws and theories. This is done with as little interruption as possible. The chapters on oxygen and hydrogen are allowed to break the thread of the story, because some knowledge of these elements and their compounds is essential early in the course to expedite the work of both the classroom and the laboratory. The author believes, however, that too often in courses in general chemistry the student is expected to grasp the meaning of chemical changes involving substances with which he is unacquainted and of which he has no basis of understanding either the composition or chemical nature. It is difficult to avoid this practice in every instance, as for example in having the student prepare oxygen from sodium peroxide or from potassium chlorate. To the end, however, that the student will not feel that chemistry is a study of isolated substances, and to the end that he may appreciate the organization of the subject matter of the science as soon as possible, the author has introduced early in the book chapters in which substances are classified and the classes described in a general way.

Instead of displacing the subject matter of what we may call classical chemistry, new information and new theories are discussed alongside the old. The aim has been to make the book thoroughly modern in treatment but not to discard anything of value on the supposition that if it belonged to the past it cannot also belong to the present and the future. Wherever there is a conflict of opinions, as for example in the presentation of the concept of an atom in terms of Dalton's theory and in terms of our present knowledge of atomic structure, or in discussing electrolytic dissociation, both the old and the new points of view are presented. If this practice serves no other purpose, it will help the student to see that chemistry is a changing, developing science and, perhaps, will cause him to realize the possibilities that lie ahead of us as we extend and revise our present knowledge of the subject.

The author has carefully attempted to give the student at all times sufficient reasons for accepting the principles and theories presented. The reader is not asked to accept statements upon faith. The author hopes that the student will ask, "Why should I believe this statement to be true?" and that the book may provide him with the answer. To be able to remember for a little while the statement of an important principle is one thing, to understand the foundation of facts upon which it is based is another and a much more important thing. All this requires space, and the book might have been considerably shortened by disregarding this motive.

Wherever definite statements of what one should believe cannot be made upon the basis of our present understanding, the student is made aware of the situation. It may be somewhat confusing not to be able to find in his text an exact statement of what matter is or a picture of exactly what an atom looks like, but this confusion is certainly no more disastrous than being led to believe something that has no factual foundation.

It is not intended that all this book should be covered in any one course. The subject matter of general chemistry is so extensive that each instructor must select those portions

he wishes to present, and hence, the text must provide the material for a variety of selections. The author has attempted to aid in this selection by having certain sections of each chapter set in smaller type. Entire chapters may be omitted in some cases. The book has been planned for use in the usual type of course, consisting of lectures, laboratory, and recitations. Certain sections of the book, such as the chapters dealing with chemical equilibrium and electrochemical cells, will require more recitational hours than others. The author hopes that the order of presentation will be found sufficiently flexible to allow the instructor to follow whatever organization of the course he thinks best. To aid in making changes in the order in which the different subjects are studied, the author has sometimes repeated material which the instructor may wish to omit when it is first presented, but which may be necessary for an understanding of sections studied at a later time. The review exercises present definite tests that the student can use to determine his own progress. The lists of reading references are not to be considered as complete. They contain titles that may be used as additional assignments or by individual students in extending their reading beyond the rather narrow boundaries of one book.

The author wishes to express his gratitude to the many companies that have provided photographs for reproduction and to the instructors and students who have used the book in its previous editions. He hopes that the changes made in this edition will improve the book's usefulness.

HERMAN T. BRISCOE

INTRODUCTION FOR THE STUDENT

BEGINNING THE STUDY OF CHEMISTRY

THE FIRST PAGES of this book will introduce you to the chemist and his work. In order that you may understand the general nature of the subject that you are to study we shall try to answer certain questions. With what kind of information is the chemist concerned? How does he work? Of what importance in the lives and affairs of men is the work that he does? Of what value to you is this study? These, we believe, are some of the questions that you would like for us to answer before you begin the study of chemistry.

SCIENCE

Chemistry is one of the fields of science, and, as compared to some of the other fields, it is a fairly recent development. The foundations of modern chemistry were laid in the late eighteenth and early nineteenth centuries. A great deal of scientific knowledge had been acquired, however, long before that time.

Science began with man's first attempts to observe and understand the world in which he lives. Very early in his history, man came to know a few simple, but unexplained and unrelated, facts. There were stars in the sky, but he did not know what they were, and if he tried to explain them at all, he probably thought of them as tiny fires lighted in each twilight and extinguished in each dawn by an unseen hand. Lightning flashes were bolts of fire thrown by evil spirits or by angry gods, and thunder was the voice of their displeasure. He knew that he must eat, but he did not know how food was used in his body. The clubs and stones he used to kill animals for food and as weapons in his struggle for existence were used, at first, as he found them; later he shaped and fashioned them better to serve his purpose.

It is not likely that he was much concerned with the extent and form of the ground he walked on, and the world must have appeared very small to him. He was completely occupied with the cares and problems which confronted him in the small place he lived in. In this respect, primitive man was like a lowly creature that crawls or creeps within a small circle, becomes acquainted with its fellow creatures as friends or foes, learns where to find its food, shelters itself by whatever means nature provides, and finally succumbs to the forces against which it is continually warring.

But man was destined to widen the circle in which he moved and to rise above the level of his fellow creatures. There developed in him certain distinguishing characteristics, best described, perhaps, by the word *intelligence*. He learned to reason about his surroundings, to find ways of circumventing the difficulties he encountered, and, in short, to combat more successfully the natural forces against which he and his fellow creatures were forced to struggle.

After his emergence from the most primitive state, man must also have had, in addition to intelligence, the longing to explore beyond familiar horizons and to learn more about himself and everything that influences his life. Very early in his history, he must have been puzzled by the stars. What are they? Where are they? He must have longed to explore the world in which he found himself. How big is it? Where does it end? He must also have wondered, at times, about himself, birth, life, and death. In short, he became a curious, observing, experimenting creature, eager to understand. The development of a written language made possible the transmission of knowledge from one generation to the next. His intelligence

and spirit of inquiry were tried and tested in numerous conflicts with natural forces, and, although not always successful, he must have emerged from each conflict better able to engage in the next and with a better understanding of nature and how it operates. Very slowly, he acquired bits of information and, putting these together, arrived at fairly satisfactory answers to some of his questions. Thus, science began.

From such meager beginnings, science has become a vast accumulation of facts and principles, the results of the careful observation, experimentation, and interpretation of many generations of men. It has grown from the few unexplained and unrelated facts known to primitive man to such proportions that no one person can, within a lifetime, grasp it all or any considerable portion of it. *As this knowledge has accumulated, it has been classified, and each fact has been put in its proper place along with other facts related to it. This organization of knowledge is science.* It is by no means a completed organization today. As long as there are questions remaining unanswered, the search for additional knowledge will continue.

Kinds of Science

The different classifications of knowledge are the different kinds of science. Astronomy is the classification concerned with the stars and other heavenly bodies — suns and their solar systems, planets and their satellites, galaxies of stars, and nebulae. Geology deals with the earth, earth-forms, and their history. Physics is concerned with the laws and principles that govern moving bodies of matter, force, work, and energy. Biology deals with the structure, growth, and reproduction of living things. Psychology, sociology, and physiology, like biology, deal with organic phenomena or the behavior of living forms of matter.

Chemistry is concerned with the properties, or characteristics, of the materials which our world and all it contains is composed of, and with the changes by which these ma-

terials are converted into others. Both chemistry and physics deal with matter and energy. Physics, more than chemistry, is concerned with the availability, nature, and effects of different forms of energy, such as heat, light, and electricity; chemistry is more concerned with different forms of matter, such as water, salt, iron, sugar, oxygen, and gold. The concern of chemistry with energy has to do with the energy changes that accompany chemical transformations of matter from one form into another. Thus, water is decomposed into hydrogen and oxygen by the expenditure of energy, when it is produced by the combination of these two forms of matter, energy is liberated. All changes of one kind of matter into another are accompanied by the adsorption or liberation of energy, usually in the form of heat.

CHEMISTRY

Its Utility

Changes in the world about him interest man because they affect the conditions under which he lives. These changes are largely chemical in character, and many of them — the fertility of soil, the weathering of rocks, decay, combustion, and other natural processes and conditions — have been the subjects of chemical studies which have added greatly to man's store of information and his ability to understand nature. By carefully applying his new knowledge, man has learned to produce many substances unknown in the natural world. In many respects, he has improved upon nature, and often he has been able to supply his needs and desires where nature fails. The results of all of these studies are described and explained in the vast literature of chemistry.

To this accumulation of knowledge there are added each year the results of several thousand investigations, some little and some great, but all of possible utility. From laboratories in industry and in the universities there is an ever-increasing flow of information concerning old and new substances,

methods by which they can be prepared, and new uses for them. We have learned to produce paper and cloth from wood, glass from sand, sugar from cornstarch, resin-like substances from carboic acid, medicines and dyes of all colors from coal-tar products, cement from shale, steel from iron, explosives from cotton, and fertilizers from the nitrogen in the air. From petroleum we have learned to produce gasoline, kerosene, vaseline, paraffin, and lubricating oils. When the demand for gasoline for automobile engines exceeded the normal yield obtainable from petroleum, we learned how to obtain more gasoline from the same quantity of crude oil. When soils became too poor to support our crops, we learned what plant foods were needed, where they could be most cheaply obtained, and how to prepare them for the plant's use. The fight against disease has called for the preparation of thousands of medicinal substances and the extraction and purification of many others of natural origin. With scarcely an exception, the materials we use in our daily lives — food, clothing, paper, glass, steel, cement, ink, drugs, dyes, soap, coal, wood, gas, gasoline, paint — all are related in some way to chemistry. Chemical principles are employed in their preparation, and their chemical properties determine their uses.

Most of you will not be chemists. But whether you become a farmer, a doctor, a banker, an engineer, a lawyer, or a housewife, there is much practical information in this study to aid you in shaping your career and making it successful. All these activities are concerned, directly or indirectly, with the materials that constitute our world. What we know of these materials and our uses of them are a part of chemistry.

The Study of Chemistry Has Other Values

In addition to its *usefulness* the study of chemistry has certain purely scientific values. Just as there are values to be derived from an understanding of how art, music, religion, and the social and political institutions of

mankind have developed, so is there value in understanding how the science of chemistry started, how it has developed, and how it has played its part in fashioning the character and extending the boundaries of modern civilization.

Our study will show how data (facts) have been collected and will describe the observations made by many investigators. It will show how these observations have been interpreted, how, from scattered facts, general laws and principles that give the science its foundation and framework have been formulated, how single bits of information have been pieced together and made to tell a story. Like the pieces of a giant "jig-saw" puzzle, these bits of information had to be found; then each had to be fitted in its proper place. As each was added the design of the picture became a little clearer.

As you study this subject, you will be called upon to follow the reasoning of others and to understand their interpretations and conclusions concerning the data they collected. You will learn what they have done by putting together for yourself the scattered bits of the "jig-saw" puzzle, just as they have put the parts together, piece by piece, all through the history of the science. Like them, you must reason clearly from individual facts to general principles — from pieces of the picture to finished parts of the final design. You must follow them even further into the unfinished portions of the picture, where pieces are missing, or if known, have not yet been assembled. As the scientist works toward the completion of his picture, he must have some plan — some reasonable and possible conception of what the unfinished portion of the picture must be. He calls this plan a *theory*, to formulate it he draws, perhaps, upon his imagination to some extent, but he is guided largely by the finished portions of the picture and by the unassembled pieces available. Using his theory as a guide, he attempts to fit these pieces, and others that may be found, into the picture in accordance with the plan he

has accepted as the most reasonable and most probable. Sometimes a reasonably supported and justified theory is lacking. Under such conditions, the scientist may follow a *hypothesis*, which is one of several possible explanations of a situation.

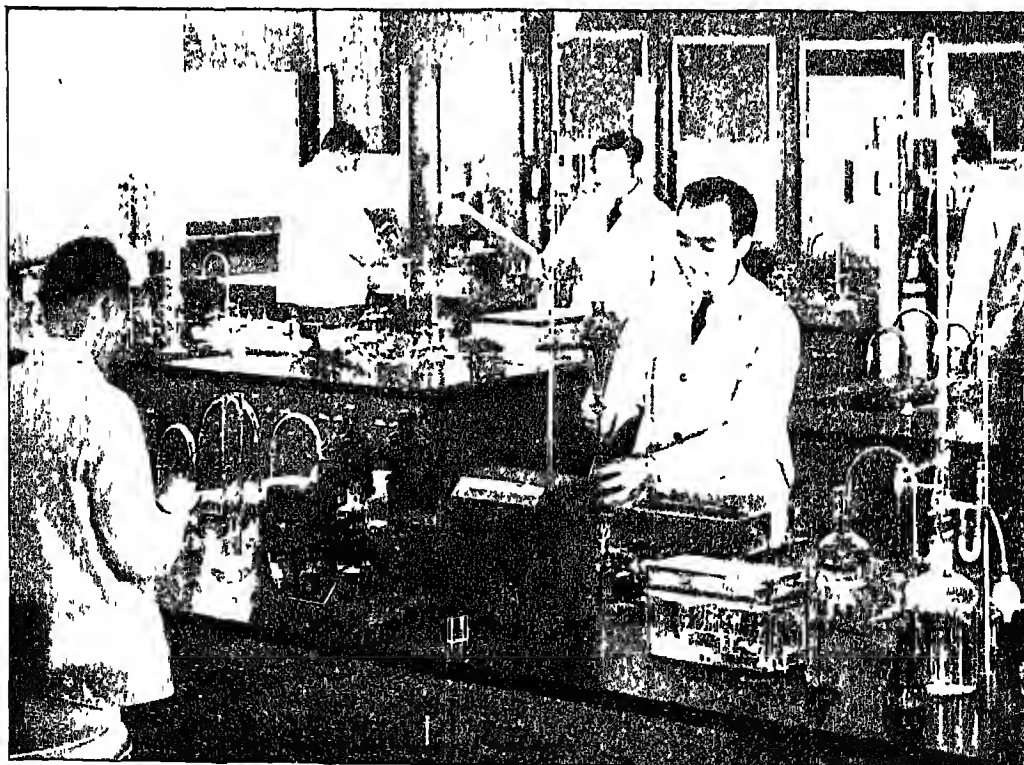
Your study of chemistry will be concerned, therefore, with *theories* as well as *laws and principles*. As you follow the development of these theories, you must learn to discriminate, you must test all suggested solutions of a problem in the light of such facts as are known; and you must modify or discard possible solutions as the facts appear to demand. You must also learn to make your own observations, to assemble and organize your data, and to arrive at your own conclusions. The study of chemistry has, therefore, other values for the student than the information it can provide about the

materials he uses and works with in his daily life.

The Methods of the Chemist

Occasionally, a great discovery in science is made accidentally; an investigator may, quite by chance, find something of importance while searching for something else, as Perkin discovered the first synthetic dye while he was seeking a way to make quinine. Most discoveries in science, however, are the results of carefully planned and outlined programs of research, aimed at definite goals and requiring hard work and patience.

In planning the study of a particular problem, in collecting his data, and finally in selecting the final solution of the problem, the chemist uses the *scientific method*. Much that has been written about this method leads one to think of it as something novel



Courtesy of Lever Brothers

Figure 1 An Industrial Laboratory

The chemical laboratory in industries is used for research, testing, and the control of the quality of products.

and peculiar to the problems of science, but there is nothing novel or strange about it. It is the simple, logical method of finding the answer to any question that can be subjected to inquiry and investigation.

We may therefore summarize the method of the scientist, as he attempts to find answers and to solve problems in his laboratory, as follows. (1) All available facts pertaining to the problem are collected. Causes and the effects to which they lead must be carefully and critically examined. (2) The facts, or data, must then be studied to discover what general relationships exist among them, and what principles can be applied to them as a whole. (3) Theories may be formulated to explain the facts upon which the general principles are based and to suggest other probable general principles that must be finally determined or rejected, before the problem is completely solved. These theories should serve as a basis for predicting, at least with some degree of accuracy, new information that may be added later; they point out the direction in which new information must be sought. In this manner, theories serve as useful guides for further work. (4) Finally, attempts must be made to establish or modify theories in such a manner that they can be accepted ultimately as general truths.

Let us consider the application of this method of attack to a single problem. What happens when a metal rusts? First, we must observe the rusting process for different metals under different conditions as to temperature, moisture, and the nature of the surrounding atmosphere. We must study the properties of the metals before and after rusting occurs. We must determine whether they gain or lose weight when they rust. We must determine whether or not they rust in a vacuum. We may even attempt to determine whether or not it is possible to convert the rust back into the metal. By such studies many facts bearing upon the problem will be collected. We find that not all metals rust under ordinary conditions, and that some do not rust under any conditions.

The rate at which rusting occurs increases as the temperature rises. Moist metals rust more rapidly than dry ones. Air appears to be necessary, because metals do not rust in its absence. We find, however, that not all of the air, but only about one fifth of it, is involved in rusting. When small pieces of iron are placed in different samples of air (in closed vessels), rusting ceases when one fifth of the air has been consumed, and *it must be consumed* in the process, because the decrease in volume can easily be measured. There is always a gain in the weight of the metal during rusting, and this gain is exactly equal to the loss in weight suffered by the air. Still other data can be secured.

From these and similar data certain conclusions can be drawn about rusting in general. For example, Rusting is a change in which a metal combines with some part of air. From the facts revealed by this study and the general conclusions resulting from it, the chemist may see justification and reason for the following theory concerning the nature and composition of the air. Air is a mixture of gases containing at least two substances, one of which is inactive and the other active in promoting the rusting of metals and probably, also, the burning of combustible materials and the process of respiration in the body. This theory is supported by a considerable number of facts, and it offers a reasonable basis for further studies of air and of other subjects, such as combustion.

Research in Chemistry

The chemist is as much concerned with the future of chemistry as he is with its history and its present state. Through research, he opens up new sources of information concerning materials, their uses and their properties. His research may be in the direction of producing new drugs, dyes, textiles, or perfumes, of improving upon methods of producing them, of finding new uses for materials, or of adding information of a general nature that does not have im-

mediate or direct practical value, but which nevertheless advances the science by extending its boundaries

We sometimes think of research as work planned and carried out to produce something that can be used — something that will have values measurable in terms of dollars and cents. Yet many of the most important studies in chemistry and in other sciences have been undertaken without any reason to believe that they would yield results of economic value. It is inevitable and desirable, of course, that all knowledge be used to man's advantage, because this is true, life has grown easier and richer as scientific knowledge and technology — the application of this knowledge to industry — have advanced. Research, however, must have no limitations, and the research worker must be free to follow whatever paths of exploration his quest may lead him to travel. Who can tell what inventions, what new conveniences, and what improvements in manufacturing may result from scientific research until the investigation is completed? Before the first electric motor was constructed, many years of seemingly useless investigation of electricity were necessary. Before proper fertilizers could be produced, research had to reveal the materials that plants require. Before indigo could be synthesized, chemistry had to grow through research on fundamental principles, until it had established methods of analysis and had given the chemist some understanding of the rules governing the changes by which one kind of material can be converted into another.

The worker in the research laboratory feels something of the same spirit of adventure that the explorer and the pioneer feel when they set out to visit new lands or to travel uncharted seas. Their explorations are of geographical frontiers, his are on the frontiers of knowledge. But like the explorer of new lands and oceans, the scientist in his laboratory acts on the impelling desire to conquer the unknown. Because of the same driving force, men try to climb Mount

Everest, to reach the poles, to explore the jungles of South America and the icy vastness of Antarctica, to climb higher into the air than anyone else has ever climbed, to reach the moon — all because these "unknowns" challenge the power, the courage, and the intellect of man.

The first glimpse through a microscope of the bacterium responsible for some disease, the sight of a newly discovered star through a telescope, or the observation of crystals of a new compound slowly forming and growing in a solution, can be just as exciting as the first sight of a newly discovered land. Geographical frontiers no longer offer many opportunities to the explorer, but the day of scientific research has only begun. There are many problems in chemistry that await solutions, some directly concerned with our needs, and some with the development of the science along general lines. With diminishing resources of petroleum, from which are produced gasoline and lubricating oils, research must provide new motor fuels. We cannot forever make paper from wood unless processes are perfected for the use of wood from rapidly growing trees. In time, it may be necessary to find new sources of energy to supply the needs of industry. New drugs must be prepared to fight disease. How can we most quickly restore the fertility of soils that have been tilled too long without thought of their future values? How do our bodies build up the complex compounds that compose them? What is the nature of the chemical forces that account for the difference between life and death? How do plants manufacture starches, sugars, and proteins? What are all the factors that determine the characteristics by which one substance can be distinguished from another?

We do not intend to overemphasize the importance of chemistry and the other sciences. There are many problems in the world, and not all of them can be solved by the methods of the scientist. We must stabilize and perfect our economic and social organizations. We must cultivate and de-

velop the arts; we must produce literature and music, and we must picture with paint and pen the beauty of the world. Without these activities, man would soon sink to the levels from which he has risen. More than all else, as the present state of the world indicates, we must in some way establish the general principles under which all men and all nations of men can live together in freedom and mutual faith.

Subdivisions of Chemistry

Just as science grew to such proportions that division into its several branches became necessary, so has chemistry grown until it now must be divided. The field is now so great that the term *chemist* tells very little about the specialized knowledge of one who has studied chemistry and who follows the subject as a profession. Instead of chemists, we have organic chemists, analytical chemists, physical chemists, inorganic chemists, and chemical engineers. Organic chemistry deals with substances composed in part of carbon, many of which are associated in some way with living bodies, plants and animals. Analytical chemistry is concerned with the identification, separation, and quantitative measurement of the composition of different substances which occur in nature or are manufactured from other materials. Physical chemistry includes the laws, principles, and theories of the subject. A knowledge of this division of the science is particularly important in all fields of chemistry, since the fundamental laws are the basis upon which all the different divisions are established. Physical chemistry includes many of the principles of physics as well as those of chemistry. Inorganic chemistry deals with substances obtained directly or indirectly from minerals, ores, and similar sources. The chemical engineer designs and operates the appliances and equipment by means of which chemical operations are carried out on an industrial scale.

This book is written for students of general chemistry, which is a survey of all the divi-

sions of the science. It deals largely, however, with fundamental principles and the sources of information from which the data supporting and suggesting these principles have been derived. Specific substances are also included in order (1) to illustrate and apply these principles intelligently, (2) to acquaint the student with the nature and variety of the chemical changes by which one form of matter is converted into another; and (3) to demonstrate by means of appropriate examples the important rôle, in general, that chemistry plays in everyday life and in industry.

Review Exercises

1. Define, in its broadest sense, the term *science*.
2. Science is sometimes classified as social science, biological science, natural science, and physical science. To what fields of knowledge do these terms apply? To which field or fields does chemistry belong?
3. With what special field of science does chemistry deal?
4. What is the value of a theory? How does a theory differ from a law?
5. What is the procedure by which the chemist arrives at conclusions and explanations of the problems he attempts to solve?
6. What is the aim and scope of a course in general chemistry?
7. In what way or for what reason is chemistry concerned with energy?
8. What are the principal subdivisions of chemistry?

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MATTER AND ENERGY

Facts are the body of science.

SAMUEL BROWN

MATTER, MASS, AND WEIGHT

1. Matter

All objects in the world about us are composed of *matter*. Although it is everywhere — in our bodies, in our houses, in city streets and in fields and forests, in the sea, in the atmosphere, in the earth, and even in far-off space — we cannot tell you what matter is. The best we can do is to make a few statements about it. Because of the matter they contain, bodies possess certain properties. They have weight; they occupy space; they possess inertia; and they can be acted upon by forces that set them in motion. We do not need to be told that matter exists in many different forms: gold, iron, copper, water, sugar, salt, and diamond, for example. Many of these, under certain conditions, can be converted into other forms. The matter in a plant, for instance, can be converted into the body-building tissues of an animal for which the plant serves as food, or the plant may die, and during its decay, a part of the matter it contains may be returned to the soil to serve as food for another plant. Forms of matter may change, but matter itself is neither destroyed nor created. We are inclined to regard it, therefore, as one of the ultimate realities of nature — a certain something that can be changed into different forms of itself but not into anything else. We think of energy as another ultimate reality.

It now seems certain that matter and energy are different forms of a single reality, and that,

under suitable conditions, one can be converted into the other. The enormous quantities of energy released by the explosion of an "atomic bomb," and by other changes of a similar nature, result from the conversion of matter into energy. There are no such changes as this in the ordinary course of events in the laboratory or in nature, or if there are, they are so small that they cannot be detected by our methods of measuring quantities of matter and energy. Hence in our elementary study of chemistry, which involves many changes of matter from one form into another, we shall regard matter as something permanent and necessary to the existence of the natural world as we know it.

2. Mass

The *mass of a body* is defined as "the quantity of matter" in the body. If we say that matter is that which possesses mass, the question becomes one of determining what mass is, and one can offer no more satisfactory answer to this than to our former question about matter. Mass, however, can be measured — at least in the sense that the mass of one body can be compared with the mass of another — because of the force of gravitation that the earth exerts upon different bodies. The attraction of the earth for a body is called the *weight* of that body; weight depends upon the quantity of matter, or mass, that the body contains and upon the distance of the body from the center of the earth. Any two objects — simple forms such as two iron bars or very complex bodies such as the moon and the earth — attract each other with a force that is inversely pro-

portional to the square of the distance between them; this attraction also depends upon the masses of the two bodies. Matter attracts matter, but the attraction of the earth for bodies on it is so much stronger than that of any of these bodies for one another that it completely overshadows the smaller gravitational effects between the bodies themselves.

Mass, also, is the property of matter that causes a body to possess *inertia*, which refers to the tendency of a body at rest to remain at rest or, if moving, to continue its motion in a straight line unless it is acted upon by outside forces. Both the inertia of a body and the gravitational attraction of the earth for the body are effects of the mass of the body and are directly proportional to it.

3 Weight

The masses of bodies are compared by *weighing*, a process by which we measure the gravitational attraction of the earth for a body by balancing it against standard "weights" for which this gravitational attraction is expressed in arbitrary units. The *chemical balance* (Figure 2) is used in the laboratory for this purpose. It consists of two pans attached to the ends of a beam that rests, at its center, upon a knife-edge. When bodies possessing the same mass are placed

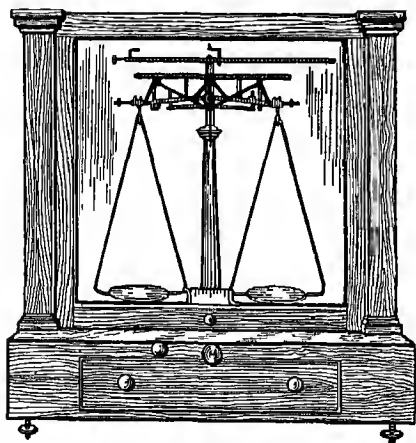


Figure 2 The Chemical Balance

on the two pans of the balance, the earth pulls each downward with the same attraction, and the beam of the balance rests in a horizontal position. The object to be weighed is placed on one pan of the balance and standard "weights" are placed on the other. The object's weight is the sum of the standard "weights" required to make the beam rest horizontally on the knife-edge. Weight is sometimes determined by means of a *spring balance*. The object to be weighed is placed in a pan attached to the end of a spring, and its weight is measured by the extent to which the spring is stretched as compared with the stretch produced by standard weights.

Although we compare the masses of two bodies by finding their weights, we should not think of *mass* and *weight* as meaning exactly the same. The attraction of the earth for a body — weight — changes with the distance of the body from the center of the earth. Thus, a body is not attracted as strongly by the earth, and does not possess the same weight, in a balloon or on a mountain, as at sea level. There is no reason, however, to believe that the *mass*, which is the quantity of matter in the body, varies from one locality to another. The weights that are used in weighing an object on the chemical balance are subject, of course, to the same changes with distance from the center of the earth as the body itself. Hence, the weight of a body is the same, when measured on this kind of balance, regardless of the locality in which it is weighed. The weight as determined by means of the spring balance, however, is not the same at all places. The same mass will stretch the spring farther at the level of the sea than on the top of a mountain, and hence the stretch of the spring by the object should be compared with the stretch by standard weights in each location where the spring balance is used.

In any work involving measurements, units must be adopted so that the quantities measured can be compared. It is for such purposes that we have introduced into everyday life such measures as bushels, barrels, hours, horsepower, pounds, tons, and kilowatts. In chemistry we are particularly concerned with units of temperature, length,

volume, and weight. We are also interested in units of energy such as heat and electricity, but these and other units will be discussed later in connection with subjects to which they are closely related.

4. Measurement of Temperature

A *thermometer* is an instrument used to measure temperature. The most common type of thermometer consists of a glass bulb filled with mercury and attached to a long capillary tube or stem. Changes in the temperature of the mercury cause it to expand or contract and therefore to rise or fall in the capillary. In the chemical laboratory, temperature is usually measured on the *Centigrade*, instead of the *Fahrenheit*, scale. The temperature at which pure water freezes is taken as zero on the Centigrade scale, the zero point on the thermometer is the point at which the level of mercury rests in the capillary when the thermometer is placed in a bath of melting ice. The boiling point of water, at what is called the average pressure of the atmosphere at sea level, is called 100°. This gives 100 equal divisions between the boiling and freezing points of water. On the Fahrenheit scale this same range of temperature is divided into 180 divisions, since on this scale water freezes at 32° and boils at 212°. The divisions are extended on either side of these two points to complete the two scales. Each division of the Fahrenheit scale is five ninths of a division on the Centigrade scale. Centigrade temperature readings can be converted into the corresponding Fahrenheit readings by means of the following formula:

$$(^{\circ}\text{F}) = (^{\circ}\text{C} - 32) \times \frac{9}{5}$$

5. Linear Measurements

The unit employed in measuring lengths or distances is the *meter*. This unit is the distance between two lines, at 0° C, on a bar of platinum and iridium deposited in the vaults of the International Bureau of

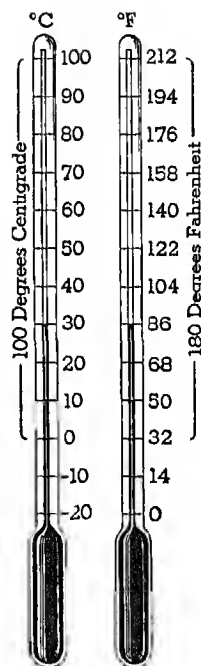


Figure 3. Comparison of the Two Temperature Scales

Weights and Measures near Paris. The meter is subdivided into *centimeters* (1 meter = 100 centimeters) and *millimeters* (1 centimeter = 10 millimeters). The abbreviations for these units are *m*, *cm*, and *mm*, respectively.

6. Measurement of Weight and Volume

The unit employed in weighing objects is the *gram* (*g*). This unit is one-thousandth part of the weight of a piece of metal containing platinum and iridium, which is deposited in the International Bureau of Weights and Measures. The weight of the entire piece of metal is, therefore, 1000 grams or one *kilogram* (*kg*). The *liter* (*l*) is the volume occupied by the quantity of distilled water which, at 4° C, will exactly balance the standard kilogram. The original idea was to select a weight of the platinum-iridium metal which would exactly balance 1000 cubic centimeters (*cc*) of pure water at 4°. This would have made one cubic centimeter of water weigh one gram. As it turned

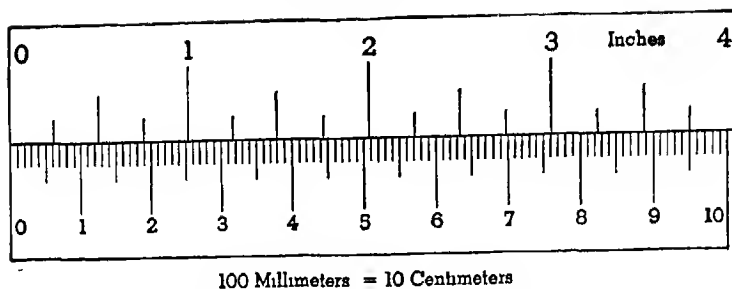


Figure 4 Lengths of Four Inches and Ten Centimeters

out, however, the weight of metal actually selected is equal to the weight of 1000 027 cubic centimeters of water at 4°. The liter representing the volume of water required to balance the standard kilogram is, therefore, not equal exactly to 1000 cc. The difference is slight and is often neglected. Instead of using the cubic centimeter as a unit in measuring small volumes, the *milliliter* (ml) is often used. This, of course, is the one-thousandth part of a liter.

7. Density

The density of any body is defined (for a definite temperature) as the mass per unit volume of the body. The volume usually selected is the cubic centimeter. Since this volume of water, at 4° C, weighs almost exactly 1 gram, the density of water is 1. The density of gold is 19.3; therefore, 1 cubic centimeter of gold weighs 19.3 grams, or 19.3 times as much as the same volume of water. Both above and below 4° C, the density of water is slightly less than 1. The densities of gases, which are very light as compared with liquids and solids, are usually expressed as the weight per liter. The temperature and pressure must be specified, however, because the density of a gas varies considerably with changes in both these conditions. The weight of a liter is called the *liter-density* and the weight of one cubic centimeter is called the *absolute density* of a gas. The densities of liquids and solids also vary under different conditions of temperature and pressure, but to a lesser extent than the density of a gas.

8. Measurement of Time

In the laboratory, time is usually measured and expressed in seconds. The mean solar day consists of twenty-four hours or 86,400 seconds. In describing experiments or natural events that occur during longer periods of time, minutes, hours, days or even years may be used.

COMPARISON OF UNITS OF MEASUREMENT

The following table may be helpful in comparing the units with which you are familiar and those of the metric system, which includes the units described above.

1 meter	is equivalent to 39.37 inches
1 centimeter	is equivalent to 0.3937 inch
0.9144 meter	is equivalent to 1 yard
1 inch	is equivalent to 2.5400 centimeters
1 liter	is equivalent to 1.0567 quarts
1 kilogram	is equivalent to 2.205 pounds
1 pound	is equivalent to 453.6 grams
1 gram	is equivalent to 15.4324 grains
1 gallon	is equivalent to 3.785 liters
1 quart	is equivalent to 0.9464 liter
1 mile	is equivalent to 1609.33 meters

The metric system is used universally in scientific work for the following reasons:

- (1) Its use is international, whereas common units of weights and measures differ from country to country and even in different trades in the same country, e.g., a baker's dozen, avoirdupois ounce, fluid ounce, etc.
- (2) Units of the metric system are related to one another as decimals; thus, the millimeter

is 0.1 of a centimeter, and the centimeter is 0.01 of a meter (3) The different units are interrelated. Thus, the gram is the weight of 1 ml of water at 4° C, and, except for the slight difference mentioned on page 12, the milliliter is equivalent to the cubic centimeter. These units are more convenient than the common system of units, in which the foot or inch is the unit of linear measurement and the pound or ounce is the unit of weight.

ENERGY

Energy is usually defined as "the capacity of a body for doing work." This definition, like that of matter, is not very satisfactory, since it associates energy with a body. Light, however, is a form of energy and is real whether it is associated with bodies of matter or not. It appears that we must consider energy as another ultimate reality in dealing with natural phenomena, it is just as real and as fundamental as matter. We have already referred (page 9) to the question of the extent to which matter and energy can be considered as separate realities.

9. Kinds of Energy

For our present purposes we can show most easily the meaning of energy by describing some of the forms in which it exists. We are familiar with heat, electricity, and light, there are several other forms.

A body may possess *potential energy* as a result of its position, condition, or composition. If any one of these is changed, the potential energy of the body is also changed. A book resting on a table possesses potential energy because of its position; in falling to the floor, it can perform work by setting into motion some other body which it strikes. A compressed spring can do work because of its potential energy, which depends upon the condition of the spring. But when the spring is released and flies back to its normal condition, and when the book falls to the floor, potential energy is converted into *kinetic energy*. Any body in

motion possesses this kind of energy, the quantity depending upon the mass (m) of the body and the square of the body's velocity (v).

$$\text{Kinetic energy} = \frac{1}{2}mv^2$$

The energy that a body possesses because of the characteristic composition, or structure, of the substance or substances that compose it is sometimes referred to as *chemical energy*. This is really a kind of potential energy stored in a substance, and under certain conditions, capable of being transformed into energy of other kinds. Cellulose, the woody material of a plant, is produced from water and carbon dioxide by a complicated series of reactions in which sunlight supplies energy that is stored in the cellulose as it is produced. When wood burns, at least a portion of this energy is released as heat, which can, in turn, be converted into mechanical energy in a steam engine.

The matter of which bodies are composed consists, we believe, of different kinds of particles arranged in patterns, and each kind of matter has its own characteristic pattern, or structure. If the forms are changed — if the structural patterns are rearranged, or even torn down and built up again in a different manner — there is a change in chemical energy. The energy of the original forms, depending as it does upon the patterns in which the particles are arranged, may be greater or smaller than that of the forms resulting from the transformations. If it is greater, there is an excess of energy after the change, and this is liberated, usually in the form of heat but sometimes as light or electrical energy. If it is smaller, there will be no change unless energy in some form, such as heat, light, or electricity, is available and can be used to produce the new patterns with their greater energy content.

10 Changes of Chemical Energy into Other Forms

Chemical energy is usually converted into

heat, or heat is converted into chemical energy, during changes in the form of matter. Hence the changes that occur in the chemical energy of a system (consisting of one or more kinds of matter) are usually measured and expressed in terms of *heat*. It is impossible to measure the total quantity of chemical energy possessed by any body of matter. Instead, we deal with the quantity of energy, in terms of heat, involved in the formation of a definite quantity of a substance from certain other substances, or in its transformation into other substances. We deal, therefore, with *changes in chemical energy* rather than the total quantities of energy possessed by different bodies of matter.

The unit of heat is the *calorie*, which is the quantity of heat required to raise the temperature of one gram of water from 15° to 16°C . (For other changes of temperature of 1° , the quantity of heat is slightly different.) The kilogram Calorie (Cal) is 1000 times as great as the calorie (cal). Changes in chemical energy during the changes of one kind of matter into another are therefore expressed as *small* or *gram* calories or as *large* or *kilogram* Calories.

11. An Example of Change in Chemical Energy

When one gram of carbon (charcoal is one form of carbon) burns, it combines with two and two-thirds grams of oxygen (from the air) to form three and two-thirds grams of a third substance called carbon dioxide. At the same time, about 8000 calories of heat are liberated for each gram of carbon. This quantity of heat will raise the temperature of approximately 80 g of water from 0° to 100°C . The release of this heat must mean that the chemical energy of the carbon dioxide produced from 1 g of carbon and $2\frac{2}{3}$ g of oxygen is less, by 8000 calories, than the chemical energy possessed by the same quantities of carbon and oxygen before they combine.

12. Conversion of Energy into Other Forms

Many transformations of energy, of course, do not involve changes in chemical composition. Mechanical energy is converted in the dynamo into electrical energy. Electrical energy is

changed in the arc light and in the incandescent lamp into light and heat, and in the motor it is changed back into mechanical energy. A body so situated that it cannot move, becomes hot when it is struck by another body which is moving with a high velocity, the kinetic energy of the moving body is converted into heat. Many other illustrations of the conversion of one form of energy into another will suggest themselves to the reader. The kinetic energy of flowing water, for example, may be converted into mechanical energy, which in turn is used to generate electricity, and this to produce still other forms, such as light and heat.

13. Units of Energy

We have already defined the calorie as the unit of heat. Other units are used to express the quantity of different kinds of energy. The unit of mechanical energy is important. This unit is the energy required to move a weight of one gram vertically through a distance of one centimeter against the force of gravity, it is called the *gram-centimeter* (g-cm). One calorie of heat is equivalent to 42,670 g-cms. One calorie represents sufficient energy, when transformed into the mechanical form, to lift a 1000 g weight 42.67 cm. or 0.4267 m. The unit of electrical energy will be discussed in a later chapter. It is called the *joule* and is equivalent to 0.23985 cal, or 1 cal is equivalent to 4.185 joules.

14. Conservation of Energy

The quantities of energy that are involved in different transformations of one form of energy into another have been studied carefully again and again. Within the limits of accuracy of the methods used to measure energy, it is quite certain that *all* the energy involved in any change appears in some form after the change is completed, none is lost, and none is gained. This principle is stated as the Law of the Conservation of Energy. *The quantity of energy involved in a transformation is constant.* This law does not mean that all the energy involved in a process can be used to do the *work* for which the

process is operated. In any transformation of energy from one form to another, only a certain quantity of the energy transformed can be made to do useful work. Not all the energy of the steam that expands in the cylinders of a locomotive can be used to move a train of cars; neither, for that matter, can all the energy available in the combustion of the coal beneath the boiler of the locomotive be used to change water into steam. Some energy is lost inevitably by the radiation of heat into the surroundings, and some is consumed in overcoming the friction of the moving parts of the machine.

DIFFERENT FORMS OF MATTER; THEIR CHANGES AND THEIR PROPERTIES

15. States of Matter

Matter exists in three states: solid, liquid, and gaseous. Water, for example, exists sometimes as a solid (ice) and sometimes as vapor (the gaseous state), although we are most familiar with its liquid state. Many kinds of matter, like water, can be obtained readily in each of the three states, for some, however, extraordinary means must be used to produce one, or even two, of the states. Common salt, for example, exists normally as a solid, at a temperature of several hundred degrees, it can be liquefied; and, at still higher temperature, it is converted into vapor. Graphite, a solid under normal conditions, can be liquefied only at 3500° – 4000° , and then only under pressure.

At the melting point, solid changes into liquid, and liquid changes into solid, at the boiling point, liquid changes into vapor, and vapor changes into liquid. Below the melting point, the solid is the stable state, above the boiling point, the vapor is stable, and between the two temperatures, the liquid is the normal state of the substance. It should be noted, however, that some substances change from the solid to the vapor state as the temperature is raised, and back again as it falls, without passing through the intermediate liquid state. This change is called *sublimation*. Furthermore, many liquids and some solids vaporize ap-

preciably — change into vapor — at all temperatures, even those far below the boiling point. Water, for example, evaporates at 0° C., and ice at lower temperatures, the rate of evaporation is not as great, of course, as it is at higher temperatures.

Changes from one state of matter to another are accompanied by changes in the energy content of the substance. When one gram of ice melts, 79 calories of heat are absorbed. When the same weight of water is changed into steam at the boiling point of water, 539 calories of heat must be absorbed. The transitions in the opposite direction — vapor to liquid and liquid to solid — are accompanied, of course, by the liberation of energy. Thus one gram of water liberates 79 calories of heat when it freezes, and when one gram of water is produced by the condensation of steam at the boiling point of water, 539 calories of heat are set free.

16. Substances; Physical and Chemical Properties

Bodies are composed of materials, such as wood, steel, porcelain, cement, stone, cloth, sulfur, gold, lead, and iron. These materials may be either *homogeneous* or *non-homogeneous*. If a material is homogeneous and has a definite (always the same) composition, it is a *substance*. All samples of a substance possess the same *properties* and have the same composition, regardless of their source. Every substance, therefore, possesses specific *physical properties*, such as color, odor, density, hardness, melting point, and boiling point. Every substance also possesses definite *chemical properties*, these concern its transformations into other substances and especially the different kinds of substances into which it can be transformed. Thus the rusting of iron, the burning of coal, and the decay of wood are all possible because of the chemical properties of the substances these materials contain. Gold does not rust and limestone does not burn because the chemical properties of these substances are different from those of iron, coal, and wood. A

substance is identified by its properties, both physical and chemical, and by its composition

In speaking of the properties of a substance, we do not include such conditions as the length, width, volume, weight, or temperature of any particular body of the substance. Such conditions are sometimes called attributes or accidental properties. They are not characteristic or specific properties of the substance in general, since they are not shown by all samples of the substance. Water at 10° and at 20°, for example, is the same substance. An iron wire 50 inches long is just as much iron as a wire 50 miles long. Sugar is the same substance, regardless of the size of the package in which it is sold by the grocer. To distribute the water contained in a barrel holding 100 gallons into twenty five-gallon portions does not change the properties of the water. Some of the specific properties of a substance depend, however, upon the conditions under which they are determined. The density of water (page 12), for example, is different for different temperatures.

A substance is defined, therefore, as a variety of matter which has definite properties and definite composition. All samples of it are identical. Water is a substance; one sample of it is like all others, and there is only one set of properties by which all samples of water can be described and identified. Natural waters from springs, wells, lakes, rivers, and oceans are not pure water, and consequently display differences in properties and composition. These differences depend upon the substances that are dissolved in the water from different sources. Copper, tin, zinc, lead, gold, salt, sugar, iron, sulfur, glycine, and oxygen are other substances.

17. Mixtures

One sample of milk is not identical, either in properties or in composition, with another, although both may be taken from the same bottle. If one sample comes from the top of a bottle that has been standing for some time, it will contain more cream than another from the lower part of the bottle. Milk,

therefore, cannot be classified as a substance, because its properties and composition are variable. Granite, cement, butter, flour, and petroleum are other examples of non-homogeneous materials, they consist of *mixtures* of substances. Thus granite is a mixture of varying quantities of silica, feldspar, and mica, each of which possesses its own set of properties. These properties are the same for silica, feldspar, and mica in granite and for separate occurrences of the three kinds of substances -- pure silica, pure feldspar, or pure mica. Wheat flour is composed principally of starch and gluten. If the flour is placed in a cloth bag and kneaded in water, the starch passes through the cloth and makes the water "milky." Gluten is left in the bag, when all the starch has been washed away. We can think of many other common materials that are mixtures rather than single substances. Coal is not a substance, because different samples contain different relative amounts, or percentages, of ash, water, carbon, and other components. Soils contain varying amounts of clay, sand, water, and organic substances resulting from the decay of vegetation. In all mixtures, the composition and characteristic properties of the component substances are unchanged.

Every material, therefore, consists of a single (pure) substance, or it is a mixture of two or more substances, each of which retains in the mixture its own characteristic properties. This is, perhaps, the most fundamental law of chemistry. It appears very commonplace and without, perhaps, any scientific value, but if we did not know that it could be applied accurately and strictly, the study of materials would be very much confused.

18. Physical and Chemical Changes

No property of a substance is more important to the chemist than the changes it can undergo, and no knowledge about the substance is more important than information concerning the conditions necessary to effect these changes.

We are aware of the many changes that occur continually around us and that alter greatly the different forms of matter with which we are acquainted. Water freezes; rocks weather and crumble, the leaves of trees change color, and fruits ripen, mountains and hills are eroded; wood decays; iron rusts, all the earth, in fact, appears to be in a continual process of change. These changes are either *physical* or *chemical*.

When physical changes occur, some of the properties of a substance may be altered for a time, *but no new substances are formed*. The following are examples of physical change: (1) The melting of ice and the condensation of steam; (2) the mixing of sugar with water to form a solution, (3) the change observed when a platinum wire is heated to redness. In each of these there is a change in properties. Thus a liquid is produced from a solid when ice melts, and a gas is changed into a liquid when steam condenses. When sugar dissolves, it too changes from the solid to the liquid state. The platinum wire changes, when heated, from a silvery, lustrous metal that reflects light to one that emits light. But there is no alteration of the fundamental character of any of these substances during these changes. Ice and steam are only the solid and gaseous states of water. Sugar dissolved in water retains its original composition and only forms a mixture, from which it is readily obtained again in its crystalline form by allowing the water to evaporate. When the platinum wire has cooled, it is the same substance and possesses the same properties as an unheated wire of the same metal, and even while it is hot it is still platinum.

A chemical change always produces at least one substance entirely different from those that existed before the change occurred. When milk sours, some of the sugar in the milk is converted into an acid, and the *properties* and *composition* of the acid are quite different from those of the sugar. Iron rust differs in many ways from iron: it contains oxygen as well as iron and is, therefore, a

different substance. Charcoal, a black solid composed almost entirely of carbon, burns in the air to form an invisible gas, which is composed of both carbon and oxygen. There is no solid residue, unless the charcoal contains non-combustible materials as impurities. In all these transformations there is a definite and radical change in the properties and composition of the substances involved.

Chemical changes are accompanied by either the absorption or the liberation of energy in some form, usually heat. Not all changes involving energy, however, are chemical. The changes of water into ice and of water into steam are physical in character, yet energy plays an important part in each of these. Energy is required to break a splinter of wood into smaller pieces. In the form of heat it is employed in heating a platinum wire to redness. Some energy is required, too, to separate the particles of sugar when this substance dissolves to form a mixture with water.

The energy changes that accompany chemical changes of matter are usually more profound, however, than those which accompany physical changes. Thus, the heat liberated when two grams of hydrogen burn to form 18 g. of water is sufficient to melt 93 g. of ice, raise the temperature of the 93 g. of water to 100° C., and change it into steam. Light as well as heat is often liberated in chemical changes. Thus when magnesium burns, the metal changes into a white powder called magnesium oxide. This change is accompanied by a very brilliant light and the liberation of considerable heat. Such effects do not attend ordinary physical changes of matter.

Review Exercises

- 1 Distinguish between the specific physical properties of a substance and the conditions, or attributes, of the substance. Use definite examples.
- 2 How is a (pure) substance different from a mixture?
- 3 How could you show that a solution of sugar in water is a mixture and not a substance?
- 4 How could you show that "tap" water is not pure water?
- 5 What are some of the physical properties of gold? of salt? of water?

6. How is a chemical change different from a physical change?
7. Under what conditions can the weights of two objects be regarded as true measures of their relative masses?
8. Why are ice, water, and water vapor not classified as three different kinds of matter — as three substances?
9. A solution of sugar in water may be homogeneous. Why can it not be classified as a substance?
10. Explain the following statement. The weight of a bar of iron is ten kilograms. What, if any, information does this statement give concerning the mass of the bar?
11. Describe a situation in which potential energy is converted into kinetic energy. Describe another situation in which kinetic energy is converted into potential energy.
12. Why are different quantities of heat liberated when equal weights of different kinds of coal are burned?
13. Give at least two reasons why each of the following must be classified as a mixture: ink, soda water, soil.
14. Are the following changes physical or chemical? The melting of ice, the rusting of iron; the conversion of cider into vinegar; the decay of wood, production of butter from cream; the boiling of water.
15. How are the meter, centimeter, and millimeter related?
16. Convert 225 centimeters to feet; 100 yards to meters, 2 miles to centimeters.
17. What is the basis of the liter as the unit of volume?
18. Convert 10 gallons to liters; 10 quarts to milliliters, and 50 milliliters to pints.
19. Convert your own weight into kilograms.
20. State the units which the following abbreviations represent: cm., g, kg., C°, l., ml., mm, m, cc.
21. The density of copper is 8.92. Calculate the weight in grams of a bar of copper 5 in. \times 3 in. \times 10 in. What is the weight of the same bar in pounds?
22. What is the volume (in cc.) of a bar of gold weighing 5 pounds?
23. The liter-density of air is 1.29. What is the weight in grams of a cubic foot of air?
24. Convert the following temperatures in the Fahrenheit scale to the corresponding Centigrade readings: 42°, 98.6°, 210°, -10°. Convert the following Centigrade readings to the corresponding Fahrenheit readings: 0°, -20°, 100°, 58°.

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KINDS OF SUBSTANCES AND THEIR CHEMICAL CHANGES

I mean by elements certain primitive and simple, or perfectly unmangled bodies.

ROBERT BOYLE

1. Introduction

In this chapter we shall learn that substances are classified as *compounds* and *elements*, and that the latter may be subdivided into *metals* and *non-metals*. We shall also be concerned with some of the different kinds of chemical changes by which substances are produced from other substances. Lastly, we shall study one or two examples of methods used in the laboratory to determine the relative weights of elements that combine to form compounds.

2. Compounds

Most substances are complex in composition and can be decomposed to form two or more simpler substances. Sometimes, the simple substances resulting from the decomposition can be made to combine again, under other conditions, to form the original complex substance. This is not always possible, however, and some complex substances are more easily produced by the combination of simple substances other than those into which they are decomposed.

Decomposition is effected by the application of heat, exposure to light, the passage of an electric current, and by other applications of energy in different forms. Thus water which contains a little acid to make it a conductor of the electric current is decomposed into hydrogen and oxygen by electricity. The silver bromide in a photographic film is decomposed by exposure to light.

When mercuric oxide, a substance bearing the same relation to mercury that iron rust bears to iron, is heated in a test tube, drops of mercury collect in the upper portions of the tube. The second substance produced by this decomposition is oxygen, an invisible gas. This gas can be detected by holding a glowing splinter of wood in the upper part of the test tube while the powder is heated, for the oxygen causes the glowing wood to burst into flame.

Water, silver bromide, and mercuric oxide can be produced directly by the combination of the same substances which they form when they decompose. Thus a mixture of hydrogen and oxygen explodes when ignited, and produces water, silver and bromine combine to form silver bromide, and mercury, when heated in the air, is converted into the red powder, mercuric oxide. Potassium chlorate is somewhat different. When heated, this substance liberates oxygen and forms a liquid, which changes to a white solid as it cools, this residue is potassium chloride. The two products of the decomposition (oxygen and potassium chloride) will not combine again to form potassium chlorate. If we wish to produce this substance, we must start with other materials.

Substances that can be decomposed into, or which can be produced by the combination of, simpler substances are called compounds. The combination by which they are produced and their decomposition are kinds of chemical change.

3. Elements

There are some substances, however, that cannot be decomposed by the methods employed to decompose compounds, and they cannot be produced by the combination of other substances in ordinary chemical changes. These substances are *elements*.

4. The Elements of the Greek Philosophers

The Greek philosophers who lived during the six centuries preceding the Christian Era believed that all bodies were composed of one, or at most four, elements. Thales believed that water was the only element. Empedocles, who lived in the fifth century B. C., and other philosophers of ancient Greece were of the opinion that fire, air, earth, and water were the elements. The reasoning that led the Greeks to such conclusions may be illustrated by the following example. Wood burns to produce fire, smoke (air), water, and ash (earth). Hence, wood must be composed of air, fire, water, and earth. Upon observing the change that occurs when ordinary water, which is not pure, is allowed to stand in an open vessel, someone might have concluded that water "changes into air" and leaves a residue of "earth." This conclusion would have led to the opinion that water must be composed of earth and air and therefore is not an element.

Aristotle discarded the four elements (air, fire, earth, and water) and substituted in

their place one primordial kind of matter, to which were added in different substances certain qualities, such as hotness, coldness, wetness, and dryness. Fire, for example, was this primordial form of matter plus the essences, or qualities, of hotness and dryness, while water contained the essences of coldness and wetness. The qualities possessed by a substance were not thought of by the Greeks as real and material in character, but they came to be considered in that way, many years later, by the alchemists. During the early centuries of the Christian Era and in the Middle Ages these qualities were looked upon as having a physical existence; and hence, it was thought that they could be added to and subtracted from different substances. If the qualities associated with primordial matter in one substance were removed and those of some other substance were added, it should be possible to change one substance into another. According to this view, it should be as easy to change one element into another as it is to change a compound into its constituent elements.

5 Alchemy and the Transmutation of the Elements

Although efforts to transmute the substances we now recognize as elements were unsuccessful, this idea was the principal objective of the alchemists. Their chief concern appears to have been the desire to

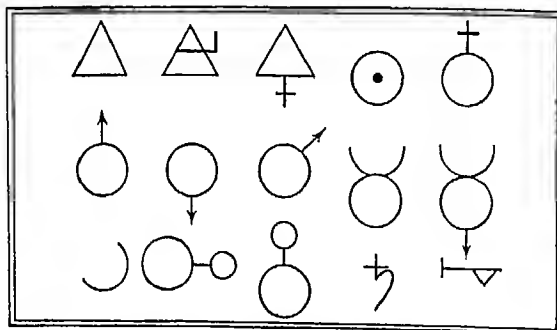


Figure 5 Symbols Used by the Alchemists
These represent (from left to right):
Top — fire, air, sulfur, gold, antimony.
Middle — zinc, copper, iron, bismuth, mercury.
Bottom — silver, arsenic, nickel, lead, water.

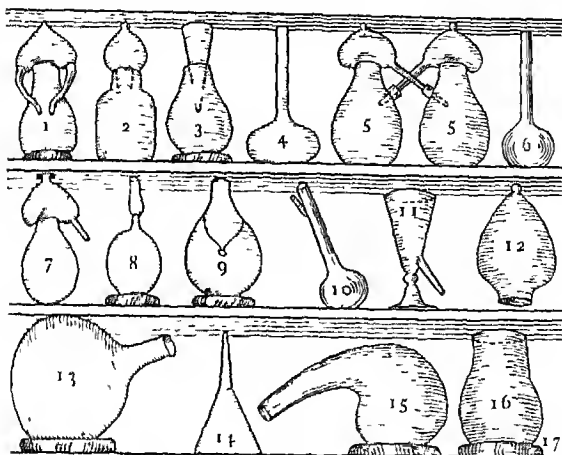


Figure 6 Apparatus Used by the Alchemists

(1) Pelican, (2) vessel for mixing; (3) Hell, (4) flat-bottomed matrass; (5) twins, (6) matrass, (7) alembic in one piece; (8) philosopher's egg; (9) egg within an egg; (10) small matrass, (11) separation glass; (12) blind alembic, (13) recipient, (14) glass funnel; (15) retort; (16) cucurbit, (17) straw mat

change the base metals, such as lead, into gold. This change appeared to be within the range of possibilities, since they believed that gold differed from lead only in possessing a few different properties and that the properties of lead could be extracted and replaced by those of gold. They made many attempts to find a mysterious something known as the "philosopher's stone." This stone, probably by some magical means, was supposed to bring about the desired transferences of properties and thus enable the alchemist to transform one substance into another at will.

Alchemy thrived during the early and middle Christian ages. Its ideas constituted the only chemistry known until the beginning of the seventeenth century and appeared now and then during the eighteenth and nineteenth centuries. Alchemy consisted, for the most part, of attempts to practice magic, charms, and various kinds of frauds. It thrived in an atmosphere of superstition, mysticism, and beliefs in the supernatural. Alchemy was not a science; it was not based on facts, and it persisted as a blind belief and a magician's art even when experimental results failed to justify it. It is strange, indeed, that failure after failure

did not convince at least some of the alchemists of the inadequacy and error of their ideas and did not encourage them to seek more satisfactory explanations of their observations.

6 Robert Boyle and His Concept of Elements

The Sceptical Chymist (1661), by Robert Boyle, brought about a radical change in scientific thought concerning the nature and composition of matter. Boyle suggested that elements are definite forms of matter that cannot be decomposed and cannot be transformed into other substances, as the alchemists thought, by transfers of essences. He showed that properties serve only to describe substances and have no material existence. He also provided the basis for the distinction of elements from compounds. He showed that to be regarded as elements, substances must resist all attempts to decompose them into or produce them from simpler ones. The substances that met this test could not be determined accurately in his day. Realizing that this was the case, Boyle insisted that substances be called elements only so long as they fully met the specifications he had set. He thus left the way clear for future in-

vestigations to correct and add to the list of elements. Boyle also showed that compounds are made by the combinations of different elements. Until the publication of his book, Aristotle's philosophy had dominated "scientific" thought, although it was not always interpreted and used as Aristotle had meant it to be. Long after 1661, the ideas and principles advanced by Boyle were not universally accepted, and it was not until late in the eighteenth century (1789) that a list of substances generally recognized as elements could be compiled. The recognition of these elements was largely the result of the work and writing of Lavoisier. The list of elements, even at the close of the eighteenth century, sometimes included "substances" such as fire and air as elements along with lead, iron, and other forms of matter.

7. Changes in the Concept of the Elements

It was once thought that the elements were quite stable and that they represented the simplest forms of matter. We know now, however, that elements can be decomposed under certain conditions — conditions that do not usually prevail in the laboratory or in nature. There is evidence, for example, that the heaviest elements, such as gold, silver, lead, and platinum — and even much lighter ones — are not stable in certain portions of the universe, as, for example, in the outer portion of the sun, where if they did exist they would be exposed to very high temperatures. Within the sun, where the temperature is extremely high, even the lightest elements are probably unstable, and matter exists only in much simpler forms, such as electrons, neutrons, and protons (page 50). These simplest forms of matter appear to be the ultimate forms from which all substances are built up in nature.

Further evidence that the elements are not to be regarded as absolutely permanent substances is found in the behavior of certain elements in the crust of our own earth. These elements, which are said to be *radioactive*, decompose spontaneously. Uranium, for in-

stance, is the first member of a long series of radioactive elements, which change from one member of the series to the next by disintegration, liberating at the same time either a second element called helium or matter negatively charged and consisting of electrons. Radioactivity is not affected in any way by the conditions of the surroundings, such as temperature. It is not within our power, therefore, to speed up or slow down the rate of the disintegration. In ordinary physical and chemical changes, these elements are not affected to any greater extent by changes in conditions than the non-radioactive elements, such as iron. Furthermore, it is not possible to make them by ordinary chemical changes, such as those employed to make compounds by the combination of simpler substances. They are, consequently, still regarded as elements, although their decomposition is a well-established fact.

Rutherford, as early as 1919, showed that some elements that are not radioactive can be decomposed if they are subjected to bombardment by particles ejected with high velocities during the disintegration of certain radioactive elements. Under this bombardment, certain elements, such as aluminum, disintegrate to form simpler substances in a manner similar to the disintegration of the radioactive elements. During recent years, other investigators have succeeded in disintegrating many elements by similar methods. This subject will be discussed later (pages 35-36).

The effect of these and other discoveries concerning the nature and behavior of matter has been to modify somewhat our conception of the elements. We do not believe, as we once did, that elements are the *ultimate* forms of matter and that they cannot be changed by decomposition into simpler forms; instead, we recognize that they are complex in structure and are composed of simpler forms. Our fundamental conception of the elements as distinguished from compounds, however, is not altered. Elements are not decomposed by chemical changes,

such as combustion, or by any of the methods commonly used to decompose compounds; also, they cannot be produced in ordinary chemical changes by the combination of other substances. They must still be regarded, therefore, as the simple kinds of matter from which compounds are formed in nature and in the laboratory.

8. Number and Abundance of the Elements

We now have definite knowledge of the existence of 96 elements. Of these all but six or seven occur either as free elements or in compounds in the earth's crust. A few of the heaviest are known only as substances produced in the laboratory from other elements. The story of the search for new elements stretches across several centuries of experimental chemistry and extends to the present day.

Only a few of the substances we now know to be elements, twelve to be exact, were known in 1630, a date which preceded Boyle's definition of an element by thirty years. These twelve elements were zinc, antimony, silver, tin, sulfur, gold, bismuth, lead, copper, iron, mercury, and carbon. Strangely enough, only two of these are among the twelve most abundant elements found in the earth's crust, which includes the outer portion of the earth, the seas, and the atmosphere.

TABLE 1

Composition of the Earth's Crust

Element	Percentage
Oxygen	50.02
Silicon	25.7
Aluminum	7.3
Iron	4.2
Calcium	3.2
Sodium	2.4
Potassium	2.3
Magnesium	2.2
Hydrogen	0.95
Titanium	0.43
Chlorine	0.21
Carbon	0.19
Other elements	0.90

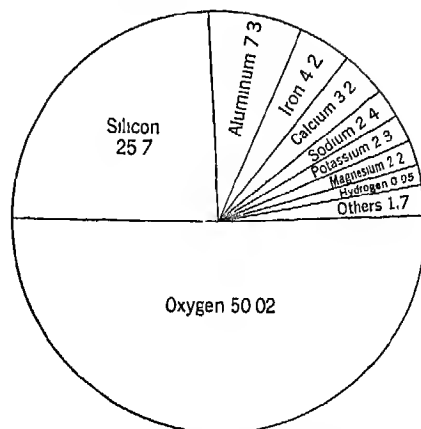


Figure 7 The Occurrence of the Elements in the Earth's Crust

Many of the less abundant elements occur here and there on or in the earth as concentrated deposits of the elements or, more frequently, of their compounds. Carbon, for example, is not widely distributed throughout the crust of the earth, but it appears in limestone and coal, in petroleum, and in the structures of plants and animals. Although it is actually a very small part of the composition of the whole earth, carbon is a very common element in our lives, because we live on the surface where it is abundant.

9 Symbols of the Elements and Names of Simple Compounds

A complete list of the elements as we now know them is given on the inside of the front cover of this book. Here, too, will be found the symbols of the elements. These are the abbreviations of the English, Latin, or German names. The names of compounds are derived usually from the names of the constituent elements. The name of a compound containing two elements includes the name of one of the elements, usually the more metallic one, and a word built upon one or more syllables of the name of the second element and ending in *-ide*. Thus, compounds of oxygen with other elements are called *oxides*, of chlorine, *chlorides*, and of nitrogen, *nitrates*. The metal magnesium, for example, forms magnesium oxide, chloride, and ni-

tride by direct combination with these three elements.

METALLIC AND NON-METALLIC ELEMENTS

At this time we cannot, of course, present the whole story of the elements. If this were possible, our book could end with this chapter. But we shall find some knowledge of the different kinds of elements very helpful in the immediately succeeding chapters, in which we attempt to show how some of the fundamental concepts of chemistry have been formulated. Naturally, these principles and theories were arrived at by experiments, in which elements and their compounds were used. To follow this discussion intelligently we must learn, first, something about the substances which were used in the experimental investigations.

The student is already familiar with several of these substances, although it is not likely that he has thought of them as elements. He knows something of gold, iron, tin, lead, copper, iodine, aluminum, silver, sulfur, oxygen, mercury, and nickel. To many students, no doubt, the names of nitrogen, zinc, platinum, chromium, radium, carbon, chlorine, hydrogen, and tungsten convey definite impressions of the substances which they represent. Many other elements, however, are strangers to most of us.

For convenience, let us classify the elements as metals and non-metals. The distinction between these two groups depends upon the chemical properties of the elements, and especially upon the properties of the compounds that the elements form with oxygen. There are, moreover, some similarities in the physical properties of the metals, the non-metals also have some physical similarities, although they differ more widely in this respect than do the metals. At this time, we shall discuss some of the general characteristics of each group.

10. The Metals

The metallic elements include gold, silver,

copper, mercury, iron, nickel, zinc, tin, lead, aluminum, and others less well known. Metals with which the student is not likely to be familiar include lithium, potassium, sodium, bismuth, antimony, magnesium, barium, calcium, cadmium, manganese, chromium, cesium, cobalt, niobium, osmium, palladium, molybdenum, strontium, and several others.

These elements are usually solids, although mercury is a liquid at ordinary temperatures. They possess luster when in a compact form, but when finely divided may lose their luster and become black. Most metals are white, but gold and copper are yellow and red, respectively. Although most metals can be beaten or rolled into sheets, a few are too brittle. Most are denser than water, although lithium, the lightest metal, is only about one half as heavy as water. The melting points of metals range from -39°C (for mercury) to temperatures in excess of 3000°C . Tungsten melts at 3370°C . Some can be vaporized at moderate temperatures, the boiling point of mercury, for example, is 357° , potassium, 760° , and sodium 880° . As a rule metals are good conductors of electricity, but the degree of conductivity varies with different metals. Copper, for example, conducts much better than iron. The metals are also good conductors of heat.

Chemically the metallic elements show little tendency to combine with one another. They combine more readily with elements which are not metals, thus they combine, usually directly, with oxygen to form oxides, with chlorine to form chlorides, and with sulfur to form sulfides. The metals differ greatly, however, in the activity they display in combining with the non-metallic elements. Lithium, sodium, potassium, rubidium, cesium, and calcium are very active metals. (An element is considered active if it combines at ordinary or moderately elevated temperatures with certain other elements which themselves are at least fairly active.) The active metals are not found in nature in their free states, because there are too

many opportunities for them to combine with oxygen and with other non-metallic elements. With few exceptions, all the metals named thus far occur naturally only in compounds, such as oxides, sulfides, and chlorides. Iron, for example, is found not in a free state but chiefly in ores that contain an oxide of iron. The pure metal is produced when the oxygen of the oxide is caused to combine with other elements, such as carbon, thus freeing the iron. If exposed to the atmosphere for some time, the pure iron changes back to the oxide, we say that it rusts or corrodes. A few metals are found in the free, or *native*, state. Their activity is so slight that they exist for ages, exposed to substances in the earth or in the atmosphere, without undergoing chemical change. The most familiar of the slightly active metals are gold, silver, platinum, and copper. All of these occur in their native state and also in certain ores as compounds.

11. The Non-Metals

Some of the non-metallic elements are solids, and some of them, such as iodine, possess a luster that gives them a slight resemblance to the metals. Boron, silicon, phosphorus, carbon, selenium, sulfur, and tellurium are solids under ordinary conditions. Bromine is a liquid at ordinary temperature. Oxygen, nitrogen, fluorine, and chlorine are gases. Helium, neon, argon, krypton, and xenon are also gaseous non-metallic elements; they are characterized by chemical inactivity and are called, therefore, the *inert gases*.

Some of the non-metals combine readily with one another. Thus, oxygen combines with carbon, sulfur, and phosphorus, when these elements burn. Chlorine, nitrogen, carbon, fluorine, sulfur, bromine, and iodine are also found in compounds with other non-metals. Thus, we may have a carbide of silicon, a sulfide of phosphorus, a chloride of carbon, and so on. On the whole, however, the non-metals combine more readily with the metals than with one another. These

combinations result in the formation of chlorides, iodides, bromides, nitrides, carbides, and fluorides of the metals. The most active of the non-metals is fluorine, which combines readily with almost all other elements.

Some elements not only have the appearance of metals but also act as metals in chemical changes in which they participate, i.e., they may form compounds similar to those formed by metals. But to a certain extent, these same elements also resemble the non-metals, especially in their compounds with oxygen or with oxygen and hydrogen. Aluminum, antimony, tin, and lead are elements of this kind. It is sometimes difficult to determine whether such elements should be classified, from a chemical point of view, as metals or as non-metals, from the physical point of view, however, they belong without question among the metals.

COMPOUNDS AND MIXTURES

12. Properties of Compounds and Mixtures Compared

Careful distinction should be made between *mixtures* of elements and *compounds* of the same elements. When elements form compounds, the properties of the elements are lost. Since a different substance is formed, the properties of a compound are entirely different from those of the elements from which it is made. Two gases, hydrogen and oxygen, combine to form water, a liquid. Chlorine, a poisonous, greenish-yellow gas, and sodium, a soft and very active metal, combine to form a white crystalline solid called sodium chloride, or salt, which is not poisonous, as ordinarily used, and has none of the marked activity of sodium. Carbon, a black solid and sulfur, a yellow solid, combine to form carbon disulfide, a colorless and very volatile liquid.

Elements or compounds can be mixed with other substances without the occurrence of chemical changes. Thus, hydrogen and oxygen can be mixed without forming water,

unless the mixture is exploded by a flame or a spark. Iron and sulfur, elements possessing very different properties, can be finely divided and mixed without losing their identity as separate substances. From the mixture, the two kinds of particles can be picked out and separated with the help of a lens, the iron particles alone can be removed by means of a magnet, or the sulfur can be separated from the iron by adding a liquid, such as carbon disulfide, in which sulfur dissolves but iron does not. On the other hand, if a mixture containing definite amounts of iron and sulfur is heated for some time, there is formed a new substance — called ferrous sulfide — which is not attracted by a magnet, cannot be separated into two kinds of particles, and does not dissolve in carbon disulfide.

always the same This law, which is called the Law of Definite Composition, is one of the most fundamental of all the laws of chemistry. By its constant composition, as well as by other properties, a compound can be distinguished from a mixture when the same substances — iron and sulfur, for example — are involved. In like manner, one compound can be distinguished from another, although we shall learn later that some compounds, although having the same composition with respect to the percentages of their constituent elements, yet differ in the manner in which the elements are combined, the difference is one of structure rather than of the kinds or quantities of the elements. Such compounds, of course, have different properties, and by these they may be identified.

13 The Composition of Compounds and Mixtures

As we have shown above, the constituents of compounds lose their identities when the compounds are produced, whereas the components of mixtures remain unchanged. Compounds are also distinguished from mixtures by their *definite compositions*. A mixture of iron and sulfur granules can have any composition, that is, the granules can be mixed in any proportion. But in the ferrous sulfide produced when the two constituent elements are heated, the ratio of the weights of iron and sulfur is always the same, 1.745 g of iron for each gram of sulfur. Common table salt, sodium chloride, likewise has a definite composition; it always contains 39.3 per cent of sodium and 60.7 per cent of chlorine, regardless of its source. Whether taken from the ocean, from Great Salt Lake, from the Dead Sea, from a deposit deep down in the earth, or from a laboratory preparation, salt always has the same composition. Similarly, the oxide of magnesium always contains 60.3 per cent of magnesium.

A compound always contains the same elements, and the ratio by weight in which these elements are combined in that compound is

14 The Chemical Energy of Compounds

It has already been stated (page 17) that every chemical change is accompanied by the liberation or absorption of energy. The quantity of energy involved in the change depends, of course, upon the total mass that participates in the change, but primarily it depends upon the substances produced and the substance or substances from which these new substances are produced. It also depends, to a lesser extent, upon the temperature at which the change occurs. For a constant temperature, at least, we may therefore say that every substance possesses a characteristic and definite quantity of chemical energy per unit of mass. This quantity cannot be measured (page 14), but we are reasonably certain that the statement is true, because the same quantity of energy, under constant conditions, is always set free or absorbed when a definite weight of any one substance is changed into a given new substance. This statement applies to all kinds of chemical changes, such as the combination of elements to form compounds or the decomposition of the compounds to form the elements.

One final item must be added to the list

of differences between compounds and mixtures. The chemical energy of a compound is not the same as the sum of the chemical energies of the elements of which it is composed. On the other hand, the total chemical energy of a mixture is equal to the sum of the energies of its parts.

We may now summarize the differences between a compound and a mixture (made from the same substances) as follows:

- (1) A compound can be separated into its constituent parts only by means of a chemical change, whereas the parts of a mixture can be separated without a chemical change.
- (2) A compound has one set of properties, but each substance in a mixture retains its own properties.
- (3) A compound has a definite composition and, at constant temperature, a definite quantity of chemical energy per unit of mass. The chemical energy of a compound differs from the sum of the energies of the elements that compose it, although, of course, its weight is equal to the sum of the weights of the elements from which it is made.

KINDS OF CHEMICAL CHANGE

The chemist usually speaks of a chemical change as a *reaction*. Substances that are changed into others are called *reactants* and are said to *react* with one another. The substances formed in the reaction are called the *products*. We shall describe four types of reactions, almost every reaction that we shall study later can be classified as belonging to one of these four types.

15 Combination

Many compounds are produced by the direct combination of elements. Iron and sulfur combine to form ferrous sulfide, magnesium, when it burns, combines with oxygen from the air to form magnesium oxide, a mixture of hydrogen and oxygen, when ex-

ploded, forms the compound we know as water.

Compounds are also produced by the combination of one compound with an element or with another compound. For example, quicklime, which is the oxide of calcium, reacts with water to form "slaked lime," or calcium hydroxide. Pure cupric sulfate, which is a white solid, combines with water to form a blue substance called *hydrated cupric sulfate*, or blue vitriol, which is the ordinary form of this substance. Carbon monoxide can combine with additional oxygen to form carbon dioxide, in which the weight of oxygen per gram of carbon is twice as great as it is in the monoxide.

16 Decomposition

When heated or when acted upon by other forms of energy, many compounds can be decomposed into simpler compounds or into their constituent elements. Thus, mercuric oxide, a compound of mercury and oxygen, evolves oxygen (a gas) when heated in a test tube, at the same time, droplets of mercury collect upon the walls in the middle and upper portions of the tube. The decomposition of certain silver compounds, when they are exposed to light, is the basis of photography. Compounds that decompose rapidly, such as nitroglycerine, are used as explosives. When sugar is heated, water is produced and evolved in the form of steam, and a charred mass containing carbon, or sugar charcoal, is left behind. When an electric current is passed through water containing a little sulfuric acid, the water is decomposed to liberate two gases, hydrogen and oxygen. *Decomposition*, the name given to this type of chemical change, is the opposite of combination. However, a substance does not always decompose to give its constituent elements. Instead of the elements, simple compounds of the elements may result. Thus, when limestone is heated, it decomposes to form an oxide of calcium, called lime, and an oxide of carbon, instead of calcium, oxygen, and

carbon, the three elements of which limestone is composed.

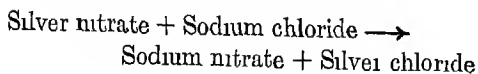
17 Replacement

This is a type of chemical change in which one substance displaces another from its compounds. Thus, a piece of iron which is placed in a solution containing a chloride of copper goes into solution, forming ferrous chloride, and the copper is thrown out of the solution as the metal. If chlorine is passed into a solution of sodium iodide (a compound formed by the combination of sodium and iodine), iodine is liberated, and when the solution is concentrated by evaporating the water, crystals of sodium chloride (common salt) are obtained.

18 Double Decomposition or Exchange

Some compounds, when brought together, change into different substances by a process (or reaction) called double decomposition. This variety of chemical change is also referred to as *metathesis* and, sometimes, as an *exchange reaction*. The latter term is appropriate, because in a reaction of this kind the parts of two compounds trade or exchange places.

The exchange reaction usually occurs in solutions. Silver nitrate and sodium chloride, when placed in the same solution, form sodium nitrate and silver chloride by double decomposition or exchange.



The silver chloride is not very soluble in water; hence, the quantity formed in excess of that which will dissolve (this amount is only 0.00016 g. in 100 ml. of water at 18° C.) is thrown out of solution. We say that silver chloride, or any other substance which is removed from a solution in this manner, is *precipitated*. The sodium nitrate that is formed at the same time remains in solution, since it is readily soluble. The solid silver chloride is removed by *filtering* the mixture through a sheet of filter paper. After the

filtrate has been evaporated to remove most of the water, crystals of sodium nitrate form as the solution cools.

The chemical changes in which a substance can take part also called the chemical *reactions* of the substance are among its most important chemical properties. The ability of magnesium to combine with oxygen, of chlorine to replace iodine, of iron to replace copper, and the tendency of mercuric oxide to decompose upon heating, are important chemical properties of these substances.

STUDIES OF TWO REACTIONS AND METHODS OF MEASURING THE COMBINING WEIGHTS OF ELEMENTS

Very little progress was made in developing the science of chemistry until methods were available for determining the composition of substances. Not only was it necessary to know what elements are combined in a given compound, but knowledge of the *percentage composition* of the substance was even more important. The study of the composition of substances belongs to the field of analytical chemistry. *Qualitative analysis* deals only with the determination of the different *kinds* of substances which can be detected. *Quantitative analysis* determines, also, the *percentage* of each substance. The quantitative study of substances owes its place of importance in chemistry to Lavoisier, who showed by his determinations of the composition of different substances that the use of the balance is one of the surest means of determining facts from which to formulate chemical principles and theories. By his analyses of many materials, Lavoisier established the general principle that during a chemical change the total quantity of matter remains unchanged. Without this principle, further progress in quantitative analysis would have been difficult and probably impossible. Berzelius later analyzed most of the compounds known in his day and contributed much information of a quantitative

character, which aided greatly in the development of other principles concerning chemical change.

We describe below two experiments which illustrate methods used in determining the composition of compounds and, specifically, the relative weights of the elements that combine to form the compounds. It should not be assumed, however, that the experiments described are applicable to all the different kinds of reactions by which compounds can be formed, or that they are applicable to the combinations of all elements.

19. Combining Proportions (by Weight) of Copper and Oxygen in Cupric Oxide

As an example of the methods used in determining the percentage composition of a substance, let us consider the composition of a compound of copper and oxygen. This compound, which is produced by passing oxygen over finely divided copper, is called cupric oxide. First, we must weigh a container for the copper; let us say that this is a small porcelain boat. Then the copper is placed in the boat and the boat and its contents are weighed. The difference between the two weights is the weight of copper used in the experiment. The boat is now placed in a glass tube (Figure 8), and while it is heated by the burner, oxygen is slowly passed over it. Oxygen can be produced, as

shown in Figure 8, by heating potassium chlorate, or some other substance that liberates oxygen when heated, in a test tube that is connected to the tube containing the boat and the copper. We must pass an excess of oxygen over the heated metal, so that none of the copper will remain unchanged. The tube is then allowed to cool, and the boat and its contents are weighed again. The red metal will have changed during the reaction to black cupric oxide, and since oxygen combines with the copper to form the oxide, there will be a gain in weight. The boat must be placed in the tube, heated, and treated with oxygen again to make certain that the reaction is complete. The reaction is considered complete when two successive weighings show that the weight of the boat and its contents is constant. We record the final weight of the boat and its contents. The difference between this and the weight of the empty boat is the weight of cupric oxide. The difference between the weights of cupric oxide and copper is the weight of oxygen which has combined with the copper.

The record of our data should look somewhat as follows:

1 Weight of boat and copper	5.232 g
2 Weight of empty boat	4.732 g
3 Weight of copper (1-2)	0.500 g
4 Weight of boat and cupric oxide	5.357 g
5 Weight of cupric oxide (4-2)	0.625 g
6 Weight of oxygen (5-3)	0.125 g

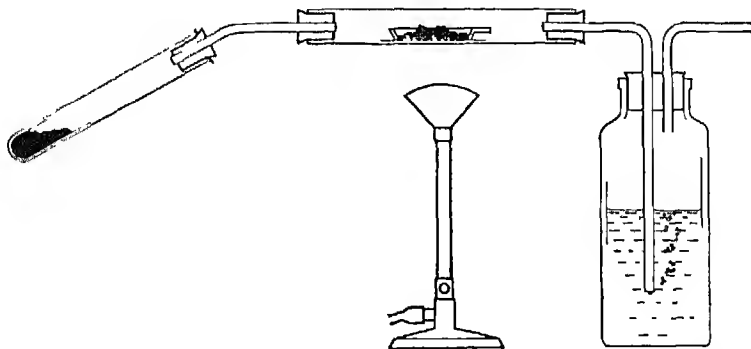


Figure 8 Determination of the Combining Proportions of Copper and Oxygen

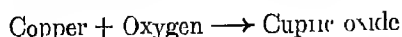
The excess of oxygen bubbles through the water in the bottle. This allows us to determine whether or not oxygen is being supplied for the reaction.

- 7 Combining proportions of copper and oxygen
 0.5 g copper 0.125 g oxygen
 1.0 g copper 0.250 g oxygen

8 Percentage of copper =
$$\frac{\text{weight of copper}}{\text{weight of cupric oxide}} = \frac{1}{1.25} \times 100 = 80$$

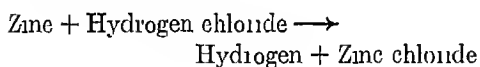
Percentage of oxygen = $100 - 80 = 20$

The chemical change in this experiment is the combination of copper and oxygen



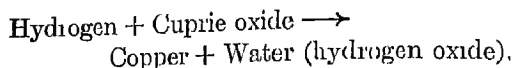
20 The Combining Proportions (by Weight) of Hydrogen and Oxygen in Water

The percentage composition of water can be determined in the following manner. Cupric oxide is placed in a boat, and the boat and its contents are weighed. The boat is then placed in a hard glass tube (Figure 9) and heated, while a stream of dry hydrogen is passed over it. In Figure 9 the bottle at the left is a hydrogen generator. It contains small pieces of zinc. A solution of hydrogen chloride is added through the funnel or thistle tube. Zinc replaces hydrogen in the hydrogen chloride



The hydrogen is dried by passing it through the tube A which is filled with calcium chloride, a substance that combines

with water but not with hydrogen. Hydrogen reacts with cupric oxide as follows:



The water produced by this reaction is in the form of steam because of the temperature in the tube B. The steam passes out of B into tube C where it is condensed and combines with the calcium chloride which that tube contains. Tube C and the calcium chloride it contains must have been weighed at the beginning of the experiment. This tube must be weighed again at the end of the experiment. The gain in weight is the weight of the water that has been produced by the reaction between cupric oxide and hydrogen. When the boat and its contents have cooled sufficiently, they are also weighed again. The loss in weight represents the weight of oxygen that has combined with hydrogen. The weight of hydrogen can be calculated as the difference between the weights of water and oxygen. The data obtained are tabulated in the following order:

- 1 Weight of boat and cupric oxide
- 2 Weight of tube C and dry calcium chloride
- 3 Weight of tube C and calcium chloride after absorption of water
- 4 Weight of water produced (3-2).
- 5 Weight of boat, copper, and cupric oxide after reaction

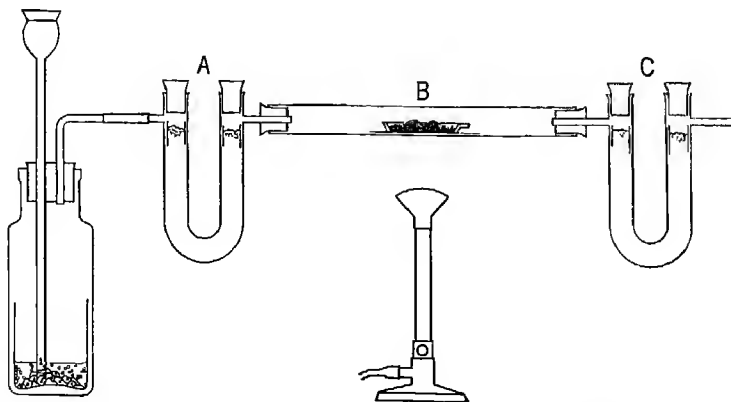


Figure 9 Determination of the Combining Proportions of Hydrogen and Oxygen

6. Weight of oxygen used (1.5)

7. Weight of hydrogen used (1.6)

$$\text{Per cent of oxygen} = \frac{\text{weight of oxygen}}{\text{weight of water}} \times 100$$

$$\text{Per cent of hydrogen} = \frac{\text{weight of hydrogen}}{\text{weight of water}} \times 100$$

The percentage composition of water is oxygen, 88.81 per cent and hydrogen, 11.19 per cent

Review Exercises

- Define element and compound. Why can each be classified as a substance?
- Under what conditions are elements disintegrated?
- Name ten metallic and ten non-metallic elements.
- What are some of the physical properties generally possessed by the metallic elements?
- If 10 g. of magnesium is burned to form the oxide, what weight of oxygen will combine with it and what weight of magnesium oxide will be formed? (See page 26.)
- A mixture containing 100 g. of finely divided iron and 75 g. of sulfur is heated. Which element and what weight of it will remain unused when the reaction is complete? (See page 26.)
- Explain why the ashes from burning wood weigh less than the wood, while the ash which remains when magnesium or iron is burned weighs more than the original metal.
- When gasoline burns there is no residue. How is this explained?
- Give examples of each of the four kinds of chemical change described in this chapter.
- The following weights of the constituent elements are combined in a sample of sulfuric acid: hydrogen, 1.5 g., sulfur, 24 g., and oxygen, 48 g. Calculate the percentage of each element in the compound.
- To what class of chemical change does each of the following reactions belong?
 - Hydrogen + Chlorine \longrightarrow Hydrogen chloride
 - Hydrogen chloride + Magnesium
Magnesium chloride + Hydrogen \longrightarrow
 - Sodium sulfide + Hydrogen chloride \longrightarrow
Hydrogen sulfide + Sodium chloride
 - Hydrogen sulfide \longrightarrow Hydrogen + Sulfur
- Classify the following materials as elements, compounds, or mixtures: aluminum, egg, paint, blood, sulfuric acid, ink, europium, mercuric oxide.
- Why have discoveries connected with radioactivity and the disintegration of elements not changed our fundamental concept of elements as distinguished from compounds?
- Explain precipitation, filtration, and filtrate.
- What weight of hydrogen can be obtained by the complete decomposition of 100 g. of water if water contains 11.19 per cent of hydrogen?

References for Further Reading

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ATOMS AND MOLECULES

It seems probable to me that God, in the beginning, formed matter in solid, massy, hard, impenetrable, moveable particles

JOHN DALTON

I Introduction

Can any substance be divided continuously and without limit into smaller and smaller particles of the same substance? Or is it possible, finally, to obtain, by division, ultimate particles — particles that cannot be further divided without destroying the identity of the substance? From the time of man's earliest thought on the nature of matter, these questions have been of fundamental interest. For many years, the arguments for an affirmative answer to the second of them — that is, in favor of the theory that every substance is composed of definite, ultimate particles — have been considered conclusive and satisfactory, and this point of view is now generally accepted as correct. It is this concept of matter that is presented in the *atomic theory*, which will be our primary concern in this chapter.

In a large measure, the atomic theory is responsible for the development of chemistry as a science. It has been a very useful guide in all studies and investigations dealing with the different forms of matter and their chemical changes. Hence the atomic theory is one of the most important subjects that you will study. As the evidence upon which the general acceptance of the theory rests is also important, we shall therefore devote considerable attention to the facts and principles that support the theory. One could, of course, accept it simply upon the assurance that scientists in general accept it. But a scientific theory can never mean very much

until one understands the foundation of facts upon which it has been built, how it explains and integrates these facts, how it has proved its usefulness, and how it can be used as a guide in new investigations.

Like all theories, the atomic theory of matter has been modified from time to time. The more important changes in our concepts of atoms will be discussed in Chapter 4. But, after a brief historical survey of some early theories, we shall take for our starting-point the atomic theory as it was proposed in the early years of the nineteenth century by Dalton. That statement of the theory was based, to a considerable extent, upon certain laws relating to chemical changes. The relationships between these laws and the theory — how the theory explains the laws and how the laws support different aspects of the theory — will be discussed at some length in this chapter. It is also important that we understand the present connotations of the terms *atom* and *molecule*, and also the scale that is used in expressing the relative weights of the atoms and molecules of different substances.

2 Particles of Matter

Many rather commonplace facts and observations give support to the atomic theory, because they can be explained satisfactorily if we assume that all forms of matter are composed of particles instead of being continuous or "all in one piece."

The flow of liquids, for example, suggests

that they are composed of particles which can move with respect to one another in somewhat the same fashion that particles of sand slip and slide over and around one another when they are poured out of a vessel. The fact that metals can be bent and beaten into thin sheets suggests a similar explanation for their composition. The tendency of one gas to pass into the space ostensibly occupied by another can be explained if we assume that each gas is composed of particles and that the particles of neither gas in fact occupy all the space. In a similar manner we can assume that particles of sugar and water are mixed in a solution of these substances, for were we to assume otherwise, we should find it difficult indeed to explain the formation of a solution. The compressibility of gases can also be explained by the assumption that they are composed of particles which can be crowded closer together by pressure. And when heated, the gas expands because the particles are further separated from one another.

The evaporation of a liquid, which occurs by degrees, a little at a time, would be difficult to explain if the substance were continuous. If it were all "in one piece"; for if it were continuous in character we might expect all of it to pass into the vapor state at the same time. If, on the other hand, the liquid is made up of particles that are more or less independent, we should expect the more rapidly moving ones that strike the surface to pass through, while those that travel more slowly remain behind. As the temperature is increased, the velocity of all the particles is increased; hence more of them are able to break through the surface and become particles of vapor.

We know that the earth's atmosphere is composed of many different substances. Why do they not separate into layers, with the heavier gases near the earth and the lighter ones above them? Perhaps because the various gases are made up of particles that move in all directions as the result of collisions, so that the different kinds of par-

ticles remain mixed instead of settling out into layers under the influence of the earth's attraction for them.

3 The First Atomic Theories

The idea that matter is discontinuous — that it is made up of particles — can be traced back as far as 1000 B. C. Some of the Greek philosophers favored this view, and one of them, Democritus, is sometimes given credit for the first atomic theory. Surprisingly enough, many of his ideas would be fairly creditable today, if they were but slightly modified. He assumed that there are as many kinds of atoms — ultimate particles — as there are varieties of matter, that is, he made no distinction between atoms of elements and "atoms" of compounds or even of mixtures, since he believed that there were atoms of wood, stone, water, iron, gold, blood, flesh, bone, air, earth, and even of the soul. By definition, therefore, the atoms of Democritus differed from the atoms with which chemistry deals today, for the atoms of modern chemistry are the ultimate particles of *elements*.

But others of the Greeks, notably Aristotle, found the atomic concept of little value in their philosophy of the natural world and of the material which composed it. They thought of all forms of matter as combinations of a fundamental substance, called *hyle*, and certain *qualities* such as wetness, dryness, cold, and heat. Because of the great influence of Aristotle and the widespread practice of alchemy, a pseudo-science which was founded in part upon his teachings, the atomic theory was abandoned for at least the first fifteen centuries of the Christian Era. During this entire period, the study of matter, along with all other scientific studies, suffered stagnation and retardation. It was not a time when men reasoned from observed effects back to their causes. Instead of observing facts as they are revealed in nature and by experiment, the alchemists clung to beliefs based upon superstition, fraud, magic, and ideas of the supernatural.

The atomic concept was revived at the time of the Renaissance. Robert Boyle and Isaac Newton were particularly prominent in bringing about this revival. But it was not until the early years of the nineteenth century that the laws of chemical combination were fairly well established, although even then they were not universally accepted. Some chemists had serious doubts about the validity of the Law of Definite Composition. Due, probably, to the lack of accurate quantitative data on the percentage composition of most substances, they were not at all certain that the composition of a compound could not be varied indefinitely.

4. Atoms and Molecules

Before beginning a detailed analysis of the atomic theory and the evidence upon which it is founded, we should understand clearly the meanings of the terms *atom* and *molecule*, as they are currently used. For these terms have not always been used in the same sense as they now are, and if we are clear as to what the modern scientist means when he speaks of atoms and molecules, we may avoid possible confusion when we see what the terms stood for in earlier statements of the atomic theory.

Atoms are the smallest portions, or particles, of elements that combine to form compounds.

Molecules are the smallest particles of any substance — element or compound — that can exist alone and that have the characteristic composition and properties of the substance. We cannot say, of course, that a single molecule of a substance has all the properties that a relatively large mass of the substance possesses. It would be absurd, for example, to speak of the boiling point of a single molecule. However, the essential chemical character — its possible reactions and the substances that can be made from it — is the same for one molecule of a substance as for a pound of the same substance.

The chemist, therefore, speaks of *atoms of oxygen* when he refers to the particles of oxygen that react with hydrogen to form

water, or with carbon to form carbon dioxide, or with any other element to form an oxide of that element. And he speaks of *molecules of oxygen* when he is referring to the smallest particles of free oxygen — of the oxygen in the air around us, for example. As we shall learn later, each molecule of oxygen, and each molecule of certain other elements, contains two atoms and is called a *diatomic* molecule. The molecules of some of the elements contain more than two atoms, and those of a few contain only one. For the latter, the molecule and the atom are one and the same particle, i.e., the molecule is *monoatomic*. The particle of water that is produced from atoms of oxygen and hydrogen is also a molecule, as we shall prove later, it contains one atom of oxygen and two of hydrogen.

DALTON'S ATOMIC THEORY

John Dalton, an English schoolmaster, is usually credited with the first statement of the atomic theory in terms that can properly be associated with the development of the science of chemistry. His conclusions about the nature of matter, published during the period from 1802 to 1808, were based upon earlier ideas regarding matter, especially those of Boyle and Newton, upon data concerning the weights of different elements that combine to form compounds; and upon his interpretation of certain phenomena — as, for example, the fact that the different gases of the atmosphere do not settle into layers. Dalton was interested in the combining proportions (by weight) of different elements, he carried out several investigations of his own, and familiarized himself with the results obtained by others. His apparatus was crude, his materials were not always pure, and his results were frequently inaccurate as judged by modern standards. Moreover, there are those who believe that he sometimes interpreted his data to agree with opinions that he had formed before carrying out his experiments. But these considerations, whatever weight they may de-

serve, should not detract from the credit due him for formulating the first comprehensive statement of a concept of matter based upon quantitative, experimental evidence. Dalton, of course, did not originate the atomic concept. As we have already pointed out, there had been others — centuries before his time — who believed all forms of matter to be composed of ultimate particles. The earlier theories, however, were entirely speculative and were unsupported by any body of quantitative data.

5 An Outline of Dalton's Theory

Dalton's theory, which he outlined in 1801, is summarized below. In some instances, his original statements have here been altered in order to make the theory agree with present knowledge. Our summary, therefore, in a certain sense, is Dalton's theory brought up-to-date.

(1) Every substance, whether element or compound, consists of ultimate particles. Dalton called all these particles atoms, from a Greek word meaning *undivided*. As now used, however, the term "atoms" (page 31) refers only to the smallest particles of elements that react to form compounds, and we shall so use the term in all of our discussions.

(2) The atoms of any one element are identical in weight and in other characteristics.

(3) Atoms cannot be divided, created, or destroyed; they are permanent, unchanging bodies.

(4) The molecules (Dalton called these "atoms," also) of a compound are produced when atoms of two or more elements combine.

(5) Atoms of elements combine in simple numerical ratios, such as one to two, or two to three, or one to one, and for any one compound this ratio is always the same.

(6) The atoms of two elements may combine in different ratios to form more than one compound. Thus, one atom of element *A* may combine with one atom of element *B* to form a molecule of the substance *AB*, and if one atom of *A* combines with two atoms of

B, a molecule of the compound *AB₂* is formed.

(7) Dalton also believed that the *most stable and the most abundant compound* of two elements consisted of particles that contained *one atom of each of the two elements*. This belief was not based on facts, and later evidence proved that it was completely unreliable.

In the absence of adequate information upon which to decide how many atoms of each of two elements combine to make a definite compound, Dalton made a reasonable, but erroneous, assumption. He thought it reasonable to assume that the compound most likely to result from the combination of two kinds of atoms would be the one formed when the atoms combined in the ratio of one to one.

6 Changes in the Concept of Atoms

Perhaps the most important difference between Dalton's concept of an atom and the concept held by modern scientists is that he thought of the atom as an *ultimate* particle of some form of matter. We are now convinced that the atom has a structure made up of different kinds of particles which are extremely small as compared to the whole.

The structure of the atom will be discussed in the next chapter. For the present, we shall briefly consider other significant changes that have been made in the atomic theory since the time of Dalton.

(1) *The atoms of an element are not identical in all cases*, as Dalton had believed. The atoms of any one element have the same, or very nearly the same, chemical properties, but they may differ in mass. Thus several kinds of lead atoms have been revealed by studies of the radioactive elements, and these have different masses. There are also two kinds of chlorine atoms, three of oxygen, three of hydrogen, and two or more of many other elements.

(2) *Atoms can be decomposed*. The atoms of radioactive elements spontaneously disintegrate, forming not only atoms of other elements, but also electrons which, so far as we know, are units, of negative electrical charge. Other kinds of atoms have been decomposed in the laboratory by bombarding them with very small, rapidly

moving particles such as those emitted by the radioactive elements

Dalton thought that the atom had no parts, that its composition was the same throughout, and that it was itself the smallest particle having this composition that could exist, hence he conceived of the atom as a particle that could not be divided or broken up into smaller parts

(3) *The most stable and abundant compound formed by two elements is not always the one in which single atoms of the two elements combine* This part of Dalton's theory was merely a guess made necessary by lack of information, and in the light of conditions at that time was probably the most reasonable guess that could have been made It was unfortunate that the development and applications of the theory, in its early years, depended so largely on the validity of this assumption Most of the errors made in the early determinations of atomic weights of the elements and the formulas of their compounds were caused by adherence to this idea.

EVIDENCE SUPPORTING DALTON'S ATOMIC THEORY

The atomic theory and the four laws discussed in the sections that follow are intimately related. We shall attempt to show how the theory explains each of these laws and the facts upon which the law is based At the same time, we shall be showing how the different parts of the theory were derived from one or more of the laws

7 Conservation of Mass

Some of the Greek philosophers believed that no portion of matter is destroyed during the changes that convert it into other forms Until about the year 1785, however, this view was not generally accepted. In that year, Lavoisier proved that *the sum of the weights of all the substances that take part in a chemical reaction is equal to the sum of the weights of all substances produced by the reaction* This is called the Law of the Conservation of Mass (Compare it with the Law of the Conservation of Energy, page 14) Lavoisier established this law by experiments in which he weighed as accurately as possible the sub-

stances involved in chemical changes such as combustion He found that mercury, for example, could be made to combine with a certain portion of air to form the red powder now known as mercuric oxide When this powder was heated, it decomposed into the same quantities of mercury and "air" as had originally combined There was no change in the total weight during the formation and decomposition of the compound We now know that the substance in the air that changes mercury into a red powder is the element oxygen In fact, it was Lavoisier himself who first recognized the existence of this element and gave it a name

Let us add one other illustration of the Law of the Conservation of Mass, explained in terms of modern information When wood burns, the hydrogen and carbon of the wood combine with oxygen in the air to form water and carbon dioxide, and the mineral matter contained in the wood is left as ash According to the Law of the Conservation of Mass, the sum of the weights of the wood and the oxygen that reacts with it is equal to the sum of the weights of ash, water, and carbon dioxide

The Law of the Conservation of Mass holds strictly for ordinary chemical reactions within the limits of accuracy of our methods of determining mass There is evidence, however, that the total mass is not constant in certain changes of an unusual character — chemical changes not of the kind usually employed in the laboratory or in industry to convert one form of matter into another For example, there is a slight reduction in total mass during the explosion of the material in an "atomic bomb," a change that involves the conversion of a heavy element into lighter elements The loss in mass amounts to about 0.1 per cent of the total This change also involves the release of large amounts of energy, and the quantity of energy released depends upon the extent to which mass is reduced It appears, therefore, that we must conclude that there is a certain degree of equivalency between matter and energy. The two laws of conservation, one of mass and the other of energy, should be combined The total mass energy content of a system

remains constant in *all* changes, and if either mass or energy disappears, an equivalent quantity of the other is produced.

There may be slight changes in mass during ordinary chemical changes, and purely theoretical reasoning gives some support to this idea. But if such changes do occur, they are so slight that they cannot be detected by the experimental methods and apparatus now available.

8. Relation of the Law of Conservation of Mass to the Atomic Theory

If atoms of elements cannot be divided, created, or destroyed during chemical changes, there can be no change in the total mass of substances participating in these changes. All that happens, evidently, is a rearrangement of the atoms in different combinations, or patterns, to form different substances. If, on the other hand, atoms were changed, or if some atoms were destroyed or created, during chemical changes, then we could not expect the combined weights of the products to be equal to the total weight of the substances participating in the change. Thus, we see that part (3) of the atomic theory (page 35) is based directly upon the principle of the conservation of mass.

9. The Law of Definite Proportions

The composition of a substance is definite. It follows, therefore, that *the proportions (by weight) of the substances that take part in a specific chemical change are definite*. Thus, iron and sulfur combine in the proportion of 63.6 per cent of iron and 36.4 per cent of sulfur to form ferrous (iron) sulfide. Magnesium oxide contains magnesium and oxygen in the ratio, by weight, of 60.32 per cent to 39.68 per cent, respectively. When hydrogen and oxygen react to form water, 1.008 g. of hydrogen combines with 8 g. of oxygen to form 9.008 g. of water. If 16 g. of oxygen is used, 2.016 g. of hydrogen is required for the complete reaction, and twice as much water as before is formed. Whenever and wherever water is formed from its elements, the ratio of the weights of the hy-

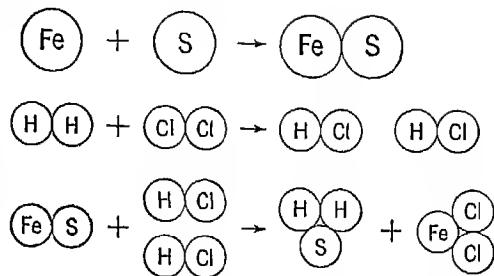


Figure 10 The Law of Conservation of Mass and the Law of Definite Proportions

The atoms of iron, sulfur, hydrogen, and chlorine are permanent and the number of each is unchanged in the reaction. All that happens is a rearrangement of the atoms to form new compounds. All of the atoms of iron are identical. So, too, are the atoms of sulfur, hydrogen, and chlorine. Furthermore, the same atoms always combine in the same ratio to make the same compounds. These statements being true, it is easy to see that the weights of ferrous sulfide and hydrogen chloride that react to produce ferrous chloride and hydrogen sulfide will always be in the same ratio to each other. We see, too, that the weight of ferrous chloride produced from a certain weight of ferrous sulfide, e.g. 1 g., will always be the same.

drogen and oxygen that combine has the same value, 1.008/8.

The principle stated above (in italics) is one of the most important in chemistry. It is called the Law of Definite Proportions. The student should note that this law does not exclude the possibility that two elements can combine in more than one proportion by weight. If they do combine in different proportions, different compounds result. Carbon and oxygen combine in different proportions to form two oxides, carbon monoxide and carbon dioxide. Water and hydrogen peroxide contain oxygen and hydrogen in two different proportions by weight. Compounds which differ in the combining proportions of the same elements will be discussed in greater detail later in this chapter.

The Law of Definite Proportions can be applied not only to elements but also to compounds, and it can be applied to the substances produced as well as to the substances that react. Thus, in the formation of water, the weights of hydrogen and oxygen are in a definite ratio, so, too, are the weights of hydrogen and water and those of oxygen and water.

10. Relation of the Law of Definite Proportions to the Atomic Theory

If all the atoms of an element are identical in mass, and if the atoms of two or more elements always combine in the same numerical ratio to form the same compound, then the proportion by weight of the elements in the compound must always be the same. On the other hand, if all the atoms of an element did *not* have the same mass, the weight of that element that combines with a definite weight of another (to form the same compound) would not always be the same, but would depend upon whether the heavier or the lighter atoms of the element took part in the reaction. The fact that the compound formed from two or more elements always has the same properties, as well as the same composition, indicates also that all the atoms of any element are identical, not only in mass, but in all their properties. If this were not so, we should expect that a compound formed by atoms having different properties would not itself always show the same set of properties.

Weight relations that appear to be exceptions to the Law of Definite Proportions have been observed in compounds of lead and, more recently, in the composition of water and other substances. Samples of lead chloride have been prepared that contain lead and chlorine in several different (approximate) ratios by weight: 207 to 71, 208 to 71, and 206 to 71. In the so-called heavy water the ratio of the weights of hydrogen and oxygen is about 2 to 8, while in ordinary water it is 1 to 8. These facts do not invalidate the Law of Definite Proportions. They indicate that there are at least three kinds of lead and two of hydrogen, and we now know that there are even more kinds of each of these elements. Each kind of lead, for example, combines with chlorine in a different ratio by weight, but for each kind of lead the combination is always in accordance with the law.

Likewise, two kinds of water are possible, because there are two kinds of hydrogen. The Law of Definite Proportions holds accurately for the combination of each variety of hydrogen with oxygen. The fault, if there is one, lies not in the

law but in our calling two different kinds of matter by the one name — hydrogen.

11. The Law of Multiple Proportions

Under different conditions, the same elements may form more than one compound. Table 2 gives the weights of each of a few elements that combine with a fixed weight of oxygen to form two or more oxides.

In the two oxides of carbon the weights of that element that combine with 16 g. of oxygen are 12 g. and 6 g., respectively. These weights of carbon are in the ratio of 2 to 1. The ratio of the weights of oxygen that combine with 1.008 g. of hydrogen to form water and hydrogen peroxide (Figure 11) are also in the ratio of 2 to 1 (16 to 8).

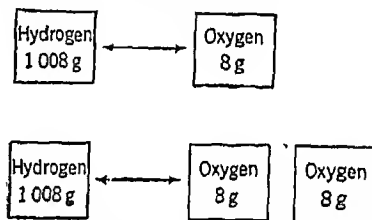


Figure 11 The Law of Multiple Proportions as Illustrated by Water and Hydrogen Peroxide

The same ratio holds for the weights of mercury that combine with 16 g. of oxygen to form two oxides of that element. In the three oxides of chlorine the weights of chlorine that combine with 16 g. of oxygen are 10.13 g., 17.73 g., and 70.92 g., respectively. Of these weights of chlorine the largest is 4 times the intermediate and 7 times the smallest weight, while the two smaller weights are in the ratio to each other of 1 to 7.

Such observations as these led John Dalton, in 1801, to formulate the Law of Multiple Proportions. *If two elements form more than one compound, the weights of one which combine with a fixed weight of the other can be represented by a ratio of small whole numbers (integers).* In less formal language, this law states, that the two weights of element A that combine with the same weight of element B to form two compounds are in the ratio of two small numbers, such as 1 to 2, 1 to 3, 2 to 3, or 3 to 4.

TABLE 2

Different Weights of the Same Elements that Combine with 16 Grams of Oxygen

Element	Weights (g) that Combine with 16 g of Oxygen	Ratios of the Weights of the Same Element that Combine with 16 g of Oxygen
Carbon	12 and 6	$12/6 = 2/1$
Copper	127.2 and 63.6	$127.2/63.6 = 2/1$
Hydrogen	2.016 and 1.008	$2.016/1.008 = 2/1$
Nitrogen	28, 14, $9\frac{1}{2}$, 7, and $5\frac{3}{5}$	$28/14 = 2/1$, $28/9\frac{1}{2} = 3/1$ $28/7 = 4/1$, $28/5\frac{3}{5} = 5/1$
Mercury	200.6 and 401.2	$401.2/200.6 = 2/1$
Chlorine	70.92, 17.73, and 10.13	$70.92/17.73 = 4/1$ $70.92/10.13 = 7/1$

As a final illustration of the law let us consider the five oxides of nitrogen. Let us take 14 g. of nitrogen as the fixed weight of one element, we then can compare the weights of oxygen that are combined with this weight of nitrogen in the five compounds.

	Nitrogen	Oxygen
(Nitrous oxide)	14	8
(Nitric oxide)	14	16
(Nitrogen trioxide)	14	24
(Nitrogen dioxide)	14	32
(Nitrogen pentoxide)	14	40

The different weights of oxygen are thus shown to be equal to 1, 2, 3, 4, and 5 times 8. They are related in the same manner as the

series of small whole numbers, 1, 2, 3, 4, 5, and are consequently in agreement with the Law of Multiple Proportions.

12 Relation of the Law of Multiple Proportions to the Atomic Theory

All the weights of element *A* that combine with a fixed weight of element *B* are multiples of the smallest weight of *A* that combines with this fixed weight of *B*. (At least all the weights of *A* are multiples of one weight, but it sometimes happens that this smallest weight itself does not combine with the fixed weight of *B* in the compounds examined.) The different weights of oxygen, for example, that combine with a fixed weight

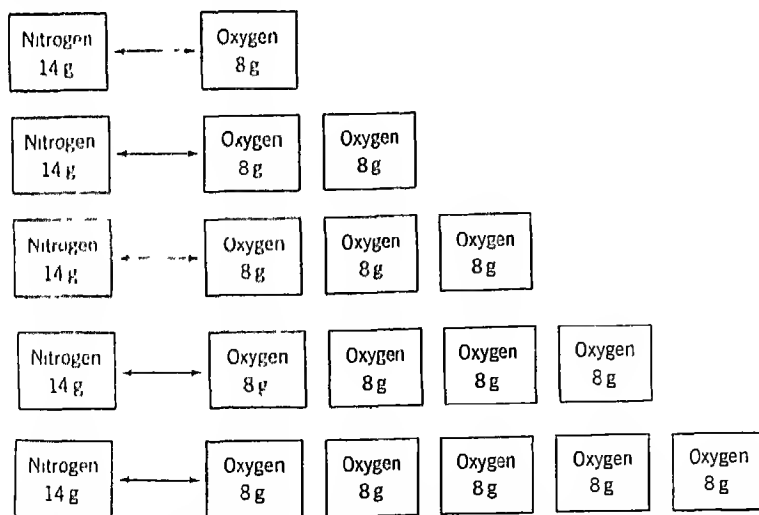


Figure 12 The Law of Multiple Proportions as Applied to the Five Compounds of Nitrogen and Oxygen

of nitrogen are 1, 2, 3, 4, and 5 times the smallest weight of oxygen that so combines. The most reasonable explanation is that twice as many atoms of oxygen combine with the same number of nitrogen atoms in the second compound as in the first, three times as many in the third, four times as many in the fourth, and five times as many in the fifth. It seems to be clearly indicated that, in combining with nitrogen, oxygen acts as if it exists in definite "packages" or units, and that, for a fixed quantity of nitrogen, one or some other whole number of these "packages" must combine. The smallest possible "packages" we may call atoms, if we wish.

In water and hydrogen peroxide, 8 g. and 16 g., respectively, of oxygen are combined with 1.008 g. of hydrogen. Since the weight of hydrogen is the same, the same number of atoms of this element must combine with 8 g. of oxygen in water and with 16 g. of oxygen in hydrogen peroxide. Now, of course, there must be twice as many oxygen atoms in 16 g. as in 8 g. Hence, the facts are satisfactorily explained, if we assume that twice as many atoms of oxygen combine with a certain number of hydrogen atoms in hydrogen peroxide as in water. If there are two hydrogen atoms for every oxygen atom in water, then there must be two oxygen atoms for every pair of hydrogen atoms in hydrogen peroxide. This is the view of modern chemical science. Dalton, however, believed that there were the same number of atoms in 1 g. of hydrogen as in 8 g. of oxygen, and hence that in water one atom of hydrogen was combined with one atom of oxygen.

13. The Law of Combining Proportions

We now must examine other data concerning the weights of different elements that combine with one another to form compounds. *Is there any relationship, for example, between the weight of carbon that combines with a certain weight of oxygen and the weight of nitrogen that combines with the same weight*

of oxygen? This is the type of question we wish to explore.

The percentage composition of a substance, such as the oxide of copper, states the number of grams of each of the elements in 100 g. of the compound, but information expressed in this manner cannot be used conveniently for comparisons of the combining proportions of different elements or of the same element in different compounds. *For these comparisons, the selection of a fixed weight of some reference element is desirable.* Comparisons of the composition of different oxides, for example, are easier to study if the weights of different elements that combine with the same weight of oxygen are considered. Any weight of oxygen, and any unit of weight, can be used, but they must be the same for each element studied. For convenience, let us take *sixteen grams of oxygen* as the standard, or reference, for the comparisons. This selection is convenient, because the weights of all the elements that combine with this weight of oxygen are greater than one gram, and at the same time none of them is large enough to make mathematical calculations very complicated. Thus we avoid dealing with extremely small or extremely large weights of any of the elements. Oxygen is selected because it combines with most of the elements, and because many of its compounds are easily produced and easily studied.

Let us now return to the question previously stated. Does any relationship exist between the weights of carbon and nitrogen that combine with the same weight of oxygen? We shall proceed to explore the answer to this question in the following series of steps.

(1) In one compound of carbon and oxygen, 12 g. of carbon combines with 16 g. of oxygen.

Whatever weight of this compound may be considered, the proportion of the weights of the two elements is always the same, namely 12 parts of carbon for every 16 parts of oxygen. If we study tons instead of grams of material, we find

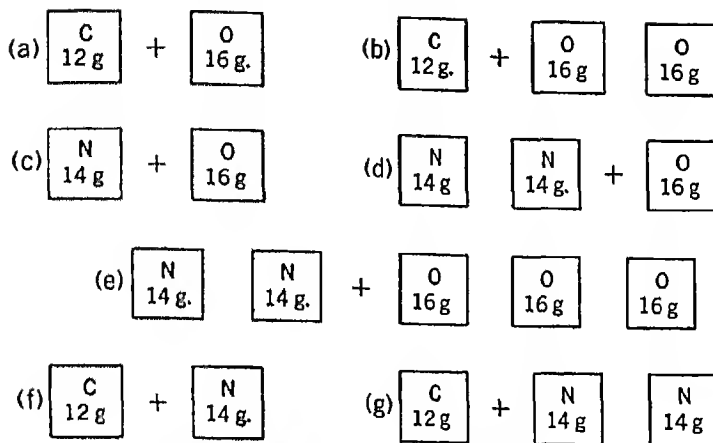


Figure 13. The Law of Combining Proportions

A few examples are shown to indicate that the ratio of the weights of carbon and nitrogen that combine, also the weights of carbon and oxygen and of nitrogen and oxygen, can be expressed by using one number for each element in all its compounds. If the weights of carbon, nitrogen, and oxygen atoms are in the proportion of 12, 14, and 16, respectively, then any weights of these elements that react will be in the ratio of 12 to 16, 14 to 16, 12 to 14, or in the ratio of multiples of these numbers, depending upon the relative numbers of atoms of each element that combine.

that 12 tons of carbon combines with 16 tons of oxygen. In a small sample, there may be 3 g. of carbon combined with 4 g. of oxygen. The important point is that the ratio of the weights of the two elements, for this compound, always has the value of 12:16, which is the same as 3:4, 6:8, 24:32, and so on.

(2) In one of the oxides of nitrogen, 14 g. of nitrogen is combined with 16 g. of oxygen.

In any quantity of this compound, whatever its size, the proportion of the weights of nitrogen and oxygen always has the same value, namely, the relation of 14:16. For example, 3.5 g. of nitrogen and 4 g. of oxygen are in the same ratio to one another as 14:16.

(3) Now let us consider the weights of carbon and nitrogen that combine with each other. In one of the compounds formed by these two elements, 14 g. of nitrogen is combined with 12 g. of carbon. In this compound, therefore, *the weights of nitrogen and carbon that combine with each other are the same that combine with 16 g. of oxygen.* This is the type of relationship that we started out to find.

(4) So far, we have considered just one compound of carbon and oxygen, one of nitrogen and oxygen, and one of carbon and

nitrogen. We must now consider the composition of other compounds containing these elements.

In all the compounds that contain carbon and oxygen, the proportion of the weights of the two elements is always 12 parts of carbon for 16 parts of oxygen, or it is 12, or some multiple of 12, parts of carbon for 16, or some multiple of 16, parts of oxygen, e.g.,

$$\frac{12}{2 \times 16}, \frac{2 \times 12}{16}, \frac{2 \times 12}{3 \times 16}, \frac{3 \times 12}{2 \times 16}, \text{ etc.}$$

In all the compounds that contain nitrogen and oxygen, the proportion of the weights of the two elements is always 14 parts of nitrogen to 16 parts of oxygen, or it is 14, or some multiple of 14, parts of nitrogen to 16, or some multiple of 16, parts of oxygen. For example, the five oxides of nitrogen have the following composition:

$$\frac{14}{16}, \frac{2 \times 14}{16}, \frac{2 \times 14}{3 \times 16}, \frac{14}{2 \times 16}, \frac{2 \times 14}{5 \times 16}$$

In each of the above fractions, the numerator represents the number of parts of nitrogen combined with 16, or some multiple of 16, parts of oxygen.

In all the compounds that contain carbon and nitrogen, the proportion of the weights of the two elements is always 12 parts of carbon for 14 parts of nitrogen, or it is 12, or some multiple of 12, parts of carbon for 14, or some multiple of 14, parts of nitrogen. Thus, the proportion of the weights of the two elements can be expressed by such ratios as

$$\frac{12}{2 \times 14}, \frac{2 \times 12}{14}, \frac{2 \times 12}{3 \times 14}, \text{ etc}$$

The facts that we have enumerated above illustrate an important general principle, sometimes called the *Law of Combining Proportions*. *In all the compounds that any element forms, the combining proportion (by weight) of that element can be expressed by a certain number or by a multiple of that number.* We have shown, for example, that, if we express the weights of oxygen as 16, or multiples of 16 parts, of that element, then the weights of any other element that combines with oxygen can be expressed by a certain number (as 12 for carbon or 14 for nitrogen) or by multiples of that number of weight units. We have also shown that the same numbers that are used in expressing the combining proportions of the different elements with oxygen can also be used to express the combining proportions of these elements with one another.

As a final illustration of this law let us consider briefly the composition of the compounds containing hydrogen and carbon. The combining proportion of hydrogen in compounds with oxygen can be expressed by using 1 008 parts of that element, or some multiple of 1 008 parts, for every 16, or some multiple of 16, parts of oxygen. Now, there are probably 300,000 compounds that contain both hydrogen and carbon. In any one of these the proportion of the combining weights of hydrogen and carbon can be expressed as

$$\frac{1\,008 \text{ parts of H}}{12 \text{ parts of C}} \quad \text{or}$$

$$\frac{\text{a multiple of } 1\,008 \text{ parts of H}}{12, \text{ or a multiple of } 12, \text{ parts of C}}.$$

A Word of Caution

Sometimes the student draws an erroneous conclusion from the Law of Combining Proportions. We have known students, for example, who believed that this law means that at least 14 parts (usually grams) of nitrogen must combine with at least 16 parts of oxygen. This, of course, is not true. Any weight of nitrogen -- 1 g. or 100 tons -- may be involved in the combination with oxygen. The law states that whatever the weight of nitrogen, the *ratio* of this weight to the weight of the oxygen with which it combines can be written as a fraction composed of 14, or some multiple of 14, for a numerator and 16, or some multiple of 16, for a denominator. Thus, 3.5 tons of nitrogen can be made to combine with 6 tons of oxygen or 3.5 milligrams of nitrogen with 6 milligrams of oxygen. Now these numbers are not 14 and 16, but the ratios of the weights of the two elements can be expressed as

$$\frac{3.5}{6} = \frac{3.5 \times 8}{6 \times 8} = \frac{28}{48} = \frac{2 \times 14}{3 \times 16}$$

The point to remember is that nitrogen and oxygen do not combine in proportions which cannot be expressed as ratios of small integral multiples of 14 and 16, respectively. Thus, we never find 5.28 g. of nitrogen combined with 7.13 g. of oxygen. The ratio 5.28/7.13 cannot be written as 14/16 or by using small integral multiples of these two numbers.

15. Relation of the Law of Combining Proportions to the Atomic Theory

This law, probably more than any other, supports the whole of the theory and parts (1), (4), and (5) particularly (see page 35). How it does so can be explained most satisfactorily by referring once again to some of the experimental data upon which the law is based.

We recall, for example, that the ratios of the weights of nitrogen and oxygen in the five oxides formed by these elements can be expressed as

$$\frac{2 \times 14}{1 \times 16}, \frac{1 \times 14}{1 \times 16}, \frac{2 \times 14}{3 \times 16}, \frac{1 \times 14}{2 \times 16}, \frac{2 \times 14}{5 \times 16}.$$

In all other compounds containing these two elements — and at least one other element as well — the ratio of the weights of nitrogen to oxygen can be expressed as some similar ratio of 14, or some multiple of 14, parts of nitrogen to 16, or some multiple of 16, parts of oxygen. We never find a compound of the two elements in which their weights cannot be expressed by such a ratio. How can these facts be explained? The atomic theory offers the following explanation:

Let us assume that nitrogen and oxygen are composed of ultimate particles — called atoms — which cannot be further divided. Let us also assume that one atom of nitrogen weighs 14, 16 as much as one atom of oxygen; or if we represent the weight of an oxygen atom by the number 16, then on the same scale the weight of a nitrogen atom is represented by 14. If this is true, *in any compound in which equal numbers of nitrogen and oxygen atoms are combined the weights of the two elements are in the ratio of 14 to 16*, regardless of the quantity of the compound considered.

In a compound for which the weights of nitrogen and oxygen are in the ratio of 2×14 to 16, the number of atoms of nitrogen is twice as great as the number of atoms of oxygen — two for one. When the ratio of the weights is 2×14 to 3×16 , nitrogen and oxygen atoms are combined in the ratio of two to three.

The student will note that the explanation given above is based upon the *assumption* that an atom of nitrogen weighs 14, 16 as much as an atom of oxygen. We might have assumed, however, that the nitrogen atom weighs 7/16 as much as the oxygen atom, upon this basis, when the elements combine in the ratio by weight of 14 to 16, we should have decided that two atoms of nitrogen are combined with one of oxygen. The only question in doubt here is the weight of the nitrogen atom as compared to the weight of an oxygen atom. This much we do know. It must be 14 weight units, or some multiple or sub-multiple of 14 weight units — 28 or 7, perhaps — as compared with 16 weight units for the atom of oxygen. The fundamental idea of the atomic theory — that each element exists in the form of

definite portions or particles that react to form compounds — is the same whether the particle of nitrogen weighs 14, 7, or some other multiple or sub-multiple of 14 weight units as compared with 16 weight units for the oxygen particle. As will be demonstrated directly, however (see page 44), there can be no doubt that the correct number for nitrogen is 14 as compared with 16 for oxygen.

ATOMIC WEIGHTS

Single atoms are too small to weigh as ordinary objects are weighed, a single atom, or even a cluster of many atoms, is too small even to be observed. The chemist, however, can compare the weights of different kinds of atoms with the weight of one atom of an element selected as a standard.

16 Definition of Atomic and Gram-Atomic Weights

The atomic weights of the elements are numbers on a scale, each number representing the relative weight of one kind of atom. As an illustration of the way this scale works, let us construct a similar scale on the same principle. Supposing that we wish to compare the weights of a large number of persons — let us say 90 persons — we might select one person whose weight, regardless of the number of pounds that he weighs, can be represented by the number 5. With 5 as the standard on our scale, the weight of a second person who is twice as heavy as the first will be represented by the number 10, the weight of another who is $8/5$ as heavy as the first, by 8, and so on, until each of the 90 persons in the group has been assigned a number that represents his weight as compared with 5 for the first individual. The scale of atomic weights is just such a scale of numbers. The number assigned to represent the weight of an oxygen atom is 16, this number serves the same purpose as the number 5 in our illustrative scale of weights.

In determining the atomic weights of different elements it is convenient, although not always necessary, to form compounds of these elements with the element selected as

Oxygen 16 g	Nitrogen 14 g	Hydrogen 1 008 g	Chlorine 35 46 g
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Figure 14

These weights of the four elements contain the same number of atoms. Hence, the relative weights of oxygen, nitrogen, hydrogen, and chlorine atoms are 16, 14, 1 008, and 35 46

the standard in the scale of comparisons. Oxygen is a suitable element to use as such a standard because it combines with many elements and because its compounds are, as a rule, easily prepared and easily studied. The weight of an atom of oxygen is represented by the number 16 — any number might have been selected — simply as a matter of convenience. This number for the oxygen atom gives a scale on which the number representing the lightest atom is slightly greater than 1, and the heaviest is approximately 240, thus the use of extremely small and extremely large numbers is avoided in calculations that involve atomic weights of elements. Furthermore, the use of 16 to represent the weight of the oxygen atom gives for many elements atomic weights that are *whole* numbers, or very nearly whole numbers.

We can now define the atomic weight of an element as a *number that represents the weight of one atom of that element as compared with the number 16 which represents the weight of an atom of oxygen*. For nitrogen the atomic weight is 14. Any weights of nitrogen and oxygen that are in the ratio of 14 to 16 contain equal numbers of atoms, because each nitrogen atom weighs 14/16 as much as one oxygen atom, hence, any number of nitrogen atoms — say 1,000,000,000 — weighs 14/16 as much as the same number of oxygen atoms. There is the same number of nitrogen atoms, for example, in 14 g of nitrogen as in 16 g of oxygen. The chemist cannot deal with individual atoms, but he sometimes must know the relative numbers of the different atoms with which he is dealing. When he uses 14 g. of nitrogen and 16 g of oxygen, he knows he is dealing with the same number of atoms of each, one atom of

nitrogen for each atom of oxygen. In most of his work, therefore, he uses weights containing the same number of atoms of different elements; when these weights are expressed in grams, they are called gram-atomic weights. *The gram-atomic weight of any element is the weight (in grams) of that element that contains the same number of atoms as 16 grams of oxygen*. For nitrogen, the gram atomic weight is 14 g.

17 Molecular and Gram Molecular Weights

Each molecule of a compound contains a definite number of atoms of each element in the compound. We should also remember that there are molecules of elements and that these may, and usually do, contain two or more atoms of the same kind. The weight of any molecule can be compared with the weight of an atom of oxygen on the same scale as the weights of different kinds of atoms. On this scale the molecular weight of a substance is a number that represents the weight of one molecule of the substance as compared with the number 16, which represents the weight of an atom of oxygen. *The gram-molecular weight of a substance (element or compound) is the weight, in grams, of the substance that contains the same number of molecules as the number of atoms in 16 g of oxygen*.

18. Why is 14 Accepted as the Correct Atomic Weight of Nitrogen?

If we could work with single molecules of compounds, we could analyze molecules of different compounds of an element — let us say, of nitrogen. In some of these molecules we would find one atom of nitrogen, and in others two, three, four, or some other number of atoms. The smallest quantity of nitrogen found in a molecule of any nitrogen compound would be one atom, and if this quantity could be weighed, we could determine the exact weight of one atom of the element. But we cannot analyze single molecules, and we cannot weigh single atoms. We can, how-

over, analyze gram-molecular weights of compounds, since these weights are of such magnitude that they can be measured accurately on the chemical balance. By such analyses, we can determine the weights of nitrogen in gram-molecular weights of its different compounds. Just as a molecule contains one, two, or some whole number of atoms, a gram-molecular weight contains one, two, or some whole number of gram-atomic weights of nitrogen. If we analyze a sufficient number of compounds in this manner, the smallest weight of nitrogen found in one gram-molecular weight of any of its compounds should be one gram-atomic weight; the weights of nitrogen in gram-molecular weights of other compounds should be multiples of this weight (1, 2, 3, or some whole number of atomic weights).

Although a full discussion of the methods used to determine the gram-molecular weights of substances must be deferred until a later chapter (see Chapter 9), we may say a few words about the subject at this time. For substances in the gaseous state, there is convincing evidence that equal volumes of different substances contain the same number of molecules, at the same temperature and pressure. Hence, the weights of single molecules of two different gaseous substances will be in the same ratio as the weights of equal volumes of the two gases. Since the molecule of oxygen contains two atoms (see page 31), the weight of the oxygen molecule is represented by the number 32 as compared to 16 which represents the weight of an atom of oxygen in the scale of relative weights of atoms, 32 g. is therefore the gram-molecular weight of oxygen.

To find the gram-molecular weight of any other gas, we need only to determine the weight of a volume of that gas equal to the volume occupied, at the same temperature and pressure, by 32 g. of oxygen.

The gram-molecular weight of a certain oxide of nitrogen, as determined by the method described above, is 30 g., and each molecule of this compound weighs, therefore, 30/16 as much as the oxygen atom. When we analyze this compound, we find that a gram-molecular weight (30 g.) of it contains 16 g. of oxygen and 14 g. of nitrogen. If we should analyze all the available compounds of nitrogen, we would find 14 grams, or some multiple of 14 grams, of nitrogen in one gram-molecular weight of each compound. As compared with 16 for oxygen, therefore, the smallest weight (the atom) of nitrogen ever found in molecular weights of its compounds is represented by the number 14, the atomic weight. This atomic weight cannot be 7 because 7 g., 21 g., 35 g., etc., of nitrogen are never found in the gram-molecular weight of any nitrogen compound. We can now understand why 14, and not 7 or some other sub-multiple or multiple of 14, is the number assigned to nitrogen in explaining the Law of Combining Proportions.

19 The Atomic Weight of Hydrogen

Having accepted 16 as the atomic weight of oxygen, we can determine the atomic weight of hydrogen by the following line of reasoning. The two elements combine in the ratio of 8 parts, by weight, of oxygen to 1.008 parts of hydrogen. We also know (see page 40) that, in forming water, two atoms of hydrogen combine with one of oxygen.

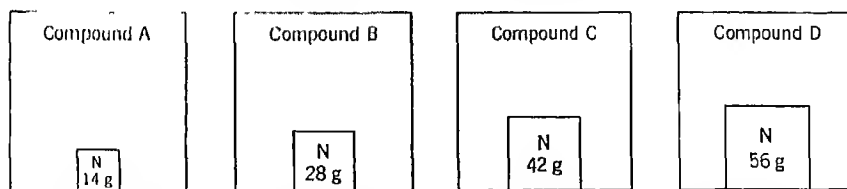


Figure 15 Weights of Nitrogen in Gram-Molecular Weights of Four Nitrogen Compounds

In a gram-molecular weight of any compound of nitrogen there is 14 g., or some multiple of 14 g. of nitrogen.
The gram-atomic weight of nitrogen, therefore, is 14 g.

This means that there must be twice as many atoms in 1 008 parts of hydrogen as there are in 8 parts of oxygen, or the same number of atoms in 1 008 parts of hydrogen and 16 parts of oxygen. Hence, if we decide to fix the atomic weight of oxygen as 16, the atomic weight of hydrogen must be 1 008 on the same scale.

As further evidence that the atomic weight of hydrogen is 1 008 we find that the smallest weight of hydrogen ever found in one gram-molecular weight of any of its compounds is 1 008 g. Thus, the molecular weight of water is 18 016. Now, as shown by analysis, 18 016 g of water contains 2 016 g of hydrogen and 16 g of oxygen. The molecular weights of other compounds contain 1 008, 3 024, 4 032, or some other multiple of 1 008 parts of hydrogen. Hence there can be no doubt that, as compared with 16 for oxygen, the weight of the smallest portion of hydrogen that reacts to form compounds must be represented by 1 008. Thus, by our definition of an atom, must therefore be the atomic weight of hydrogen.

20 Of What Value Are Atomic Weights?

The chemist uses his knowledge of the atomic weights of the elements in many ways. Let us consider two practical applications.

(1) How much oxygen must be used to convert 12 g of carbon into carbon dioxide? The chemist knows that this compound contains two atoms of oxygen for each atom of carbon. He also knows that the gram-atomic weights of carbon and oxygen are 12 g and 16 g, respectively. Therefore, he finds that for 12 g of carbon he must use 32 g of oxygen. If he labored under the erroneous impression that the atomic weight of carbon is 6, then he would make the mistake of using twice as much oxygen as he should use, because in that case he would assume that 64 g of oxygen would be required to provide twice as many atoms as are contained in 12 g of carbon.

(2) In building up, or synthesizing, a new

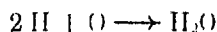
compound the chemist must know the elements that compose the compound, the number of atoms of each element in a molecule, and the structure of the compound — how the atoms are arranged in the molecules. To determine the proportions in which the atoms are combined he must know the atomic weights of the elements. To illustrate, let us assume that the analysis of methyl alcohol shows that it contains 12 parts, by weight, of carbon and 4 032 parts of hydrogen for 16 parts of oxygen. If the chemist knows that the atomic weights are 12 for carbon, 1 008 for hydrogen, and 16 for oxygen, then he also knows that for each atom of oxygen in the compound there is one atom of carbon and four of hydrogen. If, however, he labored under the mistaken idea that the atomic weight of carbon is 6 instead of 12, he would conclude that for each atom of oxygen the compound contains two atoms of carbon and four of hydrogen.

SYMBOLS, FORMULAS, AND EQUATIONS

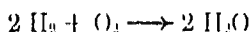
As indicated earlier in this chapter (see page 40), we know that two atoms of hydrogen combine with one atom of oxygen to produce one molecule of water. Instead of writing out a statement, as we have just done, to describe a chemical reaction, the chemist uses an *equation* consisting of certain *symbols* and *formulas*. The symbol represents one atom of the element, H stands for one atom of hydrogen. A complete list of the symbols of the elements will be found on the inside of the front cover of this book. One atom of hydrogen is represented by H, two atoms by 2 H, and so on. A formula represents a molecule. Thus, H₂ is the formula for a molecule of hydrogen, it shows that a molecule is composed of two atoms. The formula, H₂O, shows that each molecule of water is composed of two atoms of hydrogen and one atom of oxygen. As ordinarily used in the laboratory, or wherever a chemist must work with definite quantities of different substances, a symbol, such as H, repre-

sents one gram-atomic weight of an element, and a formula, such as H_2 or H_2O , one gram-molecular weight of a substance.

In equations, the formulas of the molecules of the reacting substances (the substances that we have in the beginning) are placed on the left and those of the products of the reaction are placed on the right. The number of molecules of each substance (left and right) must be such that there will be the same number of atoms of each element on both sides. We might write an equation to show the formation of water from hydrogen and oxygen as follows.



But the molecules of hydrogen and oxygen, which are the smallest particles of these elements that exist free in nature, contain two atoms each: H_2 , O_2 . The equation, therefore, should show such particles of oxygen and hydrogen, rather than single atoms, as entering the reaction.



By writing the 2 before H_2 and also before H_2O , we show that 2 molecules of hydrogen react with one molecule of oxygen to form two molecules of water. This equation is balanced because there is the same number

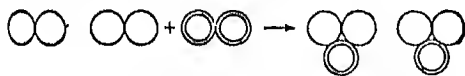


Figure 16. The Reaction of Two Molecules of Hydrogen (H_2) with One Molecule of Oxygen (O_2) to Form Two Molecules of Water, (H_2O)

of atoms of each element on each side of the equation. If the equation were not in balance, its statement would be contrary to the Law of the Conservation of Mass.

Review Exercises

- Describe an experiment by means of which the combining proportions of iron and oxygen could be determined.
- Show that the following data are in accord with the Law of Combining Proportions.

- 6 g. of carbon combines with 8 g. of oxygen to form carbon monoxide.
- 4 g. of carbon combines with $10\frac{2}{3}$ g. of oxygen to form carbon dioxide.
- 3 g. of hydrogen combines with 24 g. of oxygen to form water.
- 20 g. of carbon is combined with $6\frac{2}{3}$ g. of hydrogen in methane.
- 8 g. of carbon is combined with 2 g. of hydrogen in ethane.
- 12 g. of carbon is combined with 1 g. of hydrogen in benzene.
- 5 g. of carbon, $1\frac{1}{4}$ g. of hydrogen, and $3\frac{1}{3}$ g. of oxygen are combined in ethyl alcohol.

Assume that the numbers assigned to carbon, oxygen, and hydrogen are 12, 16, and 1, respectively.

- Show that the data of (a) and (b) of question 2 are in accord with the Law of Multiple Proportions.
- Copper forms two oxides. One of these contains 88.83 per cent of copper and the other 79.90 per cent. Show that the Law of Multiple Proportions applies to these compounds.
- Show that the combining proportions (by weight) of nitrogen and oxygen in the following compounds can be represented (without changing the values of the ratios) by using 14 parts for nitrogen and 16 parts for oxygen or integral multiples of these numbers.

COMBINING PROPORTIONS

Nitrogen	Oxygen
7	8
14	24
7	16
28	80

- Arrange the data in question 5 (without changing the values of the ratios) to illustrate the Law of Multiple Proportions.
- Distinguish between a molecule and an atom of an element.
- Summarize the evidence which indicates that matter is discontinuous rather than continuous.
- Summarize the main points in Dalton's atomic theory.
- With the help of the atomic theory, explain each of the laws of chemical combination.

11. Upon what evidence are parts 2, 4, and 5 (see page 35) of Dalton's atomic theory based?
12. Dalton believed that in water there was one oxygen atom for each atom of hydrogen. With what statement in his theory did this opinion agree?
13. If this assumption (question 12) were correct, what would be the atomic weight of hydrogen, if 16 were accepted as the atomic weight of oxygen? What would be the atomic weight of oxygen if the atomic weight of hydrogen were arbitrarily fixed at 1?
14. We now know that two atoms of hydrogen combine with each atom of oxygen in forming water. Show the line of reasoning that may be followed in finding the present accepted atomic weight of hydrogen, if 16 is taken as the atomic weight of oxygen.
15. Why is 16 for oxygen a convenient basis for the atomic weights of all the elements?
16. What do we mean when we say that the atomic weight of an element is 32?
17. What would be the atomic weight of this element (question 16) if the atomic weight of oxygen had been fixed at 64 instead of 16?
18. Why is 16 preferred to 64 as the atomic weight of oxygen in establishing a scale for the atomic weights of other elements?
19. Define atomic weight and gram-atomic weight of an element, molecular and gram-molecular weight of a compound.
20. Is there any reason why Dalton should have considered point 7 in the atomic theory (see page 35) as a likely assumption? Explain.
21. Why is 14, rather than 7 or 28, accepted as the atomic weight of nitrogen?
22. Of what value is information concerning the atomic weights of the elements?
23. Any weights of two elements that are in the same ratio as the atomic weights of the elements, contain the same number of atoms. Is this statement true? Explain.
24. Do 3.5 g of nitrogen and 4 g of oxygen contain the same number of atoms? Justify your answer.
25. What weight of nitrogen is combined with 50 grams of oxygen in a compound in which there are two atoms of nitrogen for each atom of oxygen?
23. How is the current concept of the atom different from Dalton's?

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STRUCTURES OF ATOMS AND MOLECULES

*These primitive particles, being solids, are . . .
so very hard as never to wear or break in pieces,
no ordinary power being able to divide what
God Himself made one in the first creation*

NEWTON

1 Introduction

Dalton's theory gave almost no clues to the answers for several questions about the combination of elements to form compounds and about differences in the properties of the elements themselves. These questions have not yet been answered to our complete satisfaction, but current views of the structures of atoms make possible reasonable explanations that are very useful in the study of the

elements and their compounds. Some questions of this kind that we shall be concerned with in this chapter are

(a) Why does one element not react with all others?

(b) Why does one atom of a given element react with one atom of a second, with two of a third, and with three of a fourth?

(c) How do atoms combine? What forces hold the atoms of a molecule together?

THE STRUCTURE OF THE ATOM

We cannot give here a full account of the structure of atoms or of the compounds that they form. We shall, however, summarize some of the most important structural features of atoms, as they are now understood, because some such background information will be greatly needed in the pages that follow. Further details, and particularly the evidence upon which our concepts of structure are based, together with descriptions of the methods by which such evidence has been gathered, will be left for later chapters.

2. The Structural Units of the Atom

In Dalton's day, and throughout the nineteenth century, an atom was regarded as a "simple, solid, hard, impenetrable, durable particle." We now know that an atom has a very complex, porous, and penetrable structure (Figure 17). Instead of being a

hard, solid particle, it contains (except for the hydrogen atom) three kinds of particles — *electrons*, *protons*, and *neutrons* — and these occupy only a portion of the whole space of the atom. The electron is a unit of negative electrical charge. The positively charged atom of hydrogen is a proton; the hydrogen atom contains only one electron

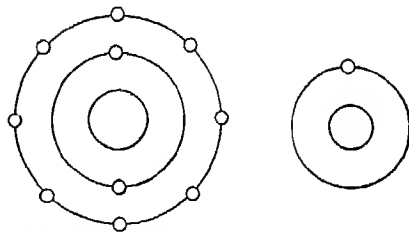


Figure 17 The Structure of an Atom of Neon (left) and of an Atom of Hydrogen (right)

The circle in the center represents the nucleus. The small circles represent planetary electrons. Those electrons in the same ring revolve in similar orbits.

and one proton, and when the electron is removed from the atom, only the proton remains. Since the electron's weight is almost negligible, the mass of the proton is very nearly equal to the mass of the hydrogen atom, the mass of the electron is only $1/1845$ as great. The electrical charge of the proton is equal in magnitude to the charge of the electron, but it has the opposite sign (+ instead of -). The neutron has no charge, and its mass is approximately equal to that of the proton.

3. General Plan of the Atom's Structure

The *nucleus* at the center of an atom contains all the protons and neutrons of the atom's structure. The nucleus of the hydrogen atom, as already stated, is one proton. The nucleus, therefore, is always positively charged, and its total charge, as compared with the charge of one electron, is equal to the number of protons that it contains. Within the nucleus protons and neutrons may exist either singly or in small groups consisting of both kinds of particles.

A sufficient number of electrons to balance the number of protons in the nucleus make up the remainder of the atom's structure. This must be true, since the atom, as a whole, is electrically neutral. The electrons make up the outer portion of the atom, and are thought to revolve in orbits of various sizes and forms, some circular and some elliptical. According to this picture, the atom resembles a miniature solar system, with the nucleus acting as the sun and the electrons as planets. The electrons and the nucleus are very small as compared with the size of the atom, which therefore, must be composed largely of empty space.

4. The Mass of an Atom

The mass of an electron is 0.00055, as compared with 16 for the mass of an atom of oxygen, the mass of a proton is 1.00758, and that of the neutron is 1.00893 on the same scale. *The mass of the atom must depend almost entirely upon the number of protons and*

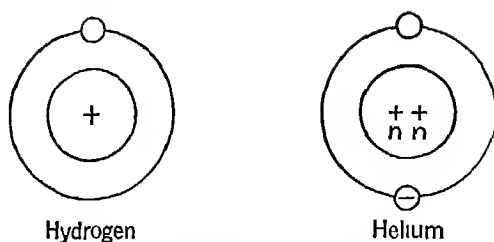


Figure 18 The Structures of Atoms of Hydrogen and Helium

neutrons in its nucleus. Since each of these particles has a mass of 1 approximately (as compared with 16 for the oxygen atom), the mass of any atom, on the same scale, is represented roughly by a number equal to the sum of the number of protons and the number of neutrons in its nucleus. This number is called the *mass number* of the element composed of this kind of atom. The atom of hydrogen is the simplest of all the atoms. Its nucleus is a single proton, and the mass of the atom (1.008) is the mass of this proton. The nucleus of the helium atom (mass 4) contains two neutrons and two protons. Similarly, we may assume that the nucleus of the oxygen atom (mass 16) contains 8 neutrons and 8 protons.

5. Atomic Numbers of the Elements

The number of units of positive charge¹ associated with the nucleus of an atom is determined by the number of protons that the nucleus contains. There are methods by which the charge of the nucleus can be determined — one of these will be described in Chapter 18 — and therefore the number of protons in the nuclei of different kinds of atoms can also be determined. It is found that this number ranges from one for the hydrogen atom to 96 for the curium atom. Hence, the element can be arranged in a series that begins with hydrogen and ends with curium and in which the atoms of any element contain one more proton each than

¹ It will be recalled that the electron carries one unit of negative charge. The charge of a proton is also one unit, but it has a + instead of a - sign.

the atoms of the preceding element. The number of an element in this series is called its *atomic number*. The atomic number of any element is the same as the number of protons in the nucleus of an atom of that element, and also the same as the number of electrons in an atom, since the number of electrons is the same as the number of protons (page 50).

6. Isotopes

On page 35 we mentioned the existence of different kinds of atoms of the same element. These atoms differ in their relative masses as compared to a mass of 16 for the atom of oxygen. For chlorine, we find two varieties of atoms, and these have masses of 34.9796 and 36.9777, values that are very close to the whole numbers 35 and 37. Similarly, there are different varieties of atoms of krypton, these have relative masses ranging from 78 to 86 (approximate). There are three varieties of the atoms of oxygen, three of hydrogen and two or more of many other elements.

The varieties of atoms that differ in atomic weight, but otherwise have identical (or very nearly identical) properties, are known as atoms of the different *isotopes* of an element. The atoms of the isotopes of an element contain the same number of protons in their nuclei and the same number of electrons. Isotopes have, therefore, the same atomic number. However, their atoms contain different numbers of neutrons, and hence they have different atomic weights. The whole number nearest the atomic weight of an iso-

topic variety of an element is called the *mass number*. It is equal to the sum of the numbers of protons and neutrons in the atomic nucleus. The structures of atoms of the two isotopes of chlorine are shown in Figure 19. The atoms of the isotope of mass number 37 contain two more neutrons than the atoms of the other isotope.

The atomic weight of an element, as calculated from data obtained by chemical methods (page 45), represents actually the average weight of all the varieties of atoms that compose the element as compared to the weight of an atom of oxygen.¹ Since the average atomic weight is constant, the different isotopes of an element must always be mixed in the same proportion, whatever the source of the element may be.

It should be noted that the average atomic weight is not simply the average of the atomic weights of the different isotopes. The number of atoms of the different isotopes must also be considered. The average atomic weight of chlorine, for example, is not the average of 35 and 37. It is a weighted average that takes into account the relative numbers of each kind of atom present in a sample of chlorine. Since the average atomic weight is 35.46, there must be approximately three atoms of mass number 35 for each atom of mass number 37 in any sample of the element.

7 The Arrangement of Electrons in the Atom

The electrons of an atom possess different amounts of energy, and therefore revolve

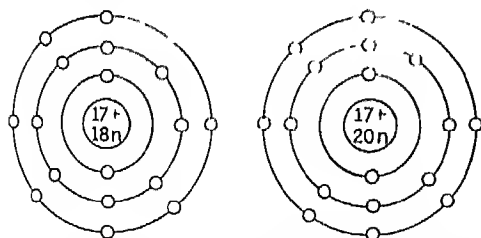


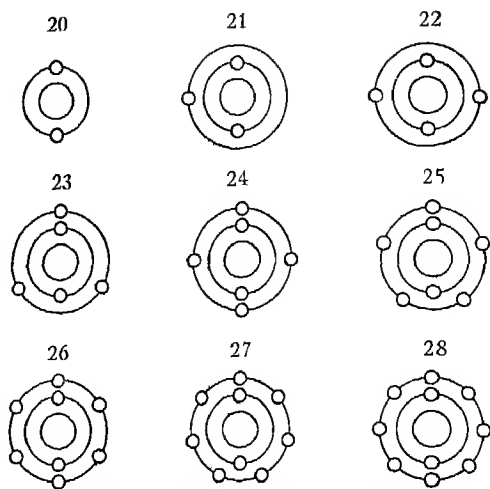
Figure 19 Atoms of the Two Isotopes of Chlorine
Because of different numbers of neutrons in the nuclei of
the two atoms the atomic weights are 35 and 37

¹ On the scale of atomic weights, the weight of an atom of oxygen is represented by the number 16. Actually, there are three isotopes of oxygen, and these have atomic weights of 16, 17, and 18. The number of atoms of the isotopes having atomic weights of 17 and 18 is so small that we may consider the average atomic weight of oxygen as 16 without introducing any serious error in the use of the scale of atomic weights for all elements. The masses of the two isotopes of chlorine as stated in Section 6 are based upon an atomic weight of 16 for the most abundant isotope of oxygen. These values are therefore slightly different from those that would be obtained if 16 were assigned as the weight of the average atom of oxygen.

around the nucleus in orbits of different size and shapes. In the normal condition of the atom, each electron possesses a definite quantity of energy and rotates in a definite orbit. In general, the normal state of the atom is one in which all the electrons of the atom are revolving in orbits that correspond to the minimum amount of energy that they can possess. If an electron absorbs energy — from a beam of X-rays, for example — it can then revolve in a larger orbit, but if this happens, the resulting state must be considered as an abnormal condition of the atom. The electron that has moved into a larger orbit — and consequently farther away from the nucleus — will tend to move back again into its original orbit, and when it does so it will release its surplus energy as light or as some other form of radiant energy.

The orbits in which the electrons of an atom rotate appear to be divided into very definite groups. For example, every atom, except the atom of hydrogen, contains two electrons that revolve in orbits of the first group, and not more than two electrons can occupy orbits of this group at the same time. These are the orbits that lie closest to the nucleus, have the smallest diameters, and contain electrons that possess the smallest amounts of energy. When we consider the atoms of lithium, which contain three electrons each, we find that the "third" electron is more easily removed from an atom than either of the other two. It must, therefore, lie farther away from the nucleus, must rotate in a larger orbit, and must possess more energy than the two other electrons. Consequently, less energy is required to separate it completely from the atom, and for that reason it is more easily removed. We say that it rotates in an orbit of the second group.

Atoms of the next seven elements, in the order of atomic numbers — beryllium, boron, and so on — contain, respectively, 2, 3, 4, 5, 6, 7, and 8 electrons in the second group; and, of course, each also contains two in the first group. (See Figures 20–28.) The orbits of the second group differ only slightly



Figures 20–28 Structures of Atoms

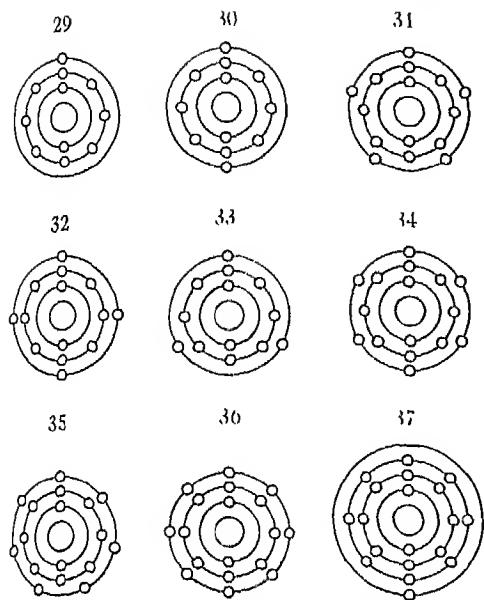
Helium (20), lithium (21), beryllium (22), boron (23), carbon (24), nitrogen (25), oxygen (26), fluorine (27), neon (28)

from one another, but they all differ a great deal from those of group one, i.e., their diameters are considerably greater. The electrons in these orbits possess much more energy and are more easily removed from the atoms than the two electrons of the first group. The second group appears to be filled when it contains eight electrons, as it does in the atom of neon. We reach this conclusion because the structure of this atom appears to be very stable, and because in the atom that contains one more electron — sodium, Figure 29 — the additional electron appears to enter an orbit that belongs to a third group. It is much more easily removed from the atom than any of the eight electrons of the second group or either of the two in the first group.

As more and more electrons are added in the heavier atoms, other groups of orbits are filled. See Table 3 and Figures 29–37.

The number of electrons required to fill each of the first four groups is shown below.

Group	Maximum No. of Electrons in the Group
1	2
2	8
3	18
4	32



Figures 29-37 Structures of Atoms

Sodium (29), magnesium (30), aluminum (31), silicon (32), phosphorus (33), sulfur (34), chlorine (35), argon (36), potassium (37)

For convenience only, it is customary to show the electrons that rotate around the nucleus in similar orbits -- that belong to the same group -- as small circles located on a common ring, or circle, as shown in Figure 37. We should keep in mind, however, that each electron rotates in its own orbit, and that these orbits lie in different planes, instead of the single plane used in our diagrams. Since electrons rotating in different orbits possess different quantities of energy, we sometimes refer to the different groups of orbits in which electrons rotate about the nucleus as the different energy levels of the atom.

8. Distribution of Electrons in Atoms Containing More than Two Groups

For group one, it appears that the maximum number of electrons that may be present is two. For group two, the maximum number is eight. A group of eight electrons appears to have a high degree of stability, and the behavior of atoms and all other available information indicates that *the out-*

most group of electrons of any atom cannot contain more than this number

Hence, as soon as the outside group has eight electrons in it, as it does in neon, the next electrons go into the next higher group (Figures 29-37). It will also be noted (Figure 37) that, as soon as the third group contains eight electrons, the next electron goes into an orbit of group four, although the third group is not filled completely until it contains eighteen electrons. The next electron (calcium) also goes into the fourth group (see Table 3), but in the atoms of the next several elements (scandium to zinc) the additional electrons go into group three until the number in that group reaches eight, and the group is filled. The next six electrons (gallium to krypton) join the two electrons already located in the fourth group until the total number in that group is eight, the maximum number that can be located in an outermost group. The next two electrons go into orbits of the fifth group (rubidium and strontium). Table 3 shows the distribution of electrons in the different levels of the atoms of the first forty elements. The structures of other elements are discussed in Chapter 18.

9 One Way in which Atoms may React to Form Compounds

When atoms of one element react with the atoms of one or more other elements to form a compound, it is the electrons in the outermost levels of the atoms that are involved in the change¹. In these reactions each atom tends to change in such a way that a stable outermost group of electrons will be produced. This stability may be obtained by some atoms if they lose to others all the electrons in their outermost group, thus leaving as the exterior portion of their structures the stable arrangement of electrons already existing in the next lower group. For example, an atom of lithium can attain stability by

¹ For some elements, such as copper for which the distribution is 2-8-18-1 (Table 13), an electron in the group next to the outside one may be involved.

TABLE 3
Distribution of Electrons in Atomic Energy Levels

Element	Atomic Number	Number of Electrons in Different Levels					
		1	2	3	4	5	6
Hydrogen	1	1					
Helium	2	2					
Lithium	3	2	1				
Beryllium	4	2	2				
Boron	5	2	3				
Carbon	6	2	4				
Nitrogen	7	2	5				
Oxygen	8	2	6				
Fluorine	9	2	7				
Neon	10	2	8				
Sodium	11	2	8	1			
Magnesium	12	2	8	2			
Aluminum	13	2	8	3			
Silicon	14	2	8	4			
Phosphorus	15	2	8	5			
Sulfur	16	2	8	6			
Chlorine	17	2	8	7			
Argon	18	2	8	8			
Potassium	19	2	8	8	1		
Calcium	20	2	8	8	2		
Scandium	21	2	8	9	2		
Titanium	22	2	8	10	2		
Vanadium	23	2	8	11	2		
Chromium	24	2	8	13	1		
Manganese	25	2	8	13	2		
Iron	26	2	8	14	2		
Cobalt	27	2	8	15	2		
Nickel	28	2	8	16	2		
Copper	29	2	8	18	1		
Zinc	30	2	8	18	2		
Gallium	31	2	8	18	3		
Germanium	32	2	8	18	4		
Arsenic	33	2	8	18	5		
Selenium	34	2	8	18	6		
Bromine	35	2	8	18	7		
Krypton	36	2	8	18	8		
Rubidium	37	2	8	18	8	1	
Strontium	38	2	8	18	8	2	
Yttrium	39	2	8	18	9	2	
Zirconium	40	2	8	18	10	2	

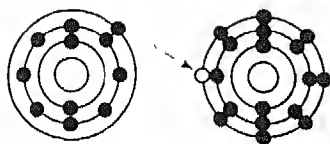


Figure 38 The Reaction of an Atom of Sodium with an Atom of Chlorine
One electron is transferred

losing the single electron that it has in group two, thus leaving on its external surface the two electrons of group one. Similarly, the sodium atom will lose its single electron of group three, leaving exposed to external influences the stable group of eight electrons in group two.

If one atom in a reaction loses electrons, it must do so because some other atom takes them away from it, and hence we must assume that certain atoms can attain stability by acquiring electrons. These are the atoms that already have almost enough electrons to produce a stable outermost group. The fluorine atom, for example, contains seven electrons in group two. It can attain stability if it acquires one more from an atom that has only one in its outermost group, for example, and thus produces a group of eight. The hydrogen atom with only one electron can produce a stable group containing two electrons by removing an electron from some other atom, usually, however, the hydrogen atom loses its electron to some other atom. Helium with two electrons in group one, neon with eight in group two,

and argon with eight in group three already possess stable outermost groups, and then atoms, therefore, show almost no tendency to react with others.

Thus, in their reactions, some atoms will lose electrons and others will acquire them. The number of electrons that an atom loses or gains depends upon the number in the outermost group of the atom. If this group contains one, two, or three electrons, the atom is more likely to lose these to other atoms that attract them than it is to acquire a sufficient number to complete the group of eight, which is, usually, the number that can occupy orbits in the outermost group. If, on the other hand, the outermost group contains six or seven electrons, the tendency to acquire, from other atoms, two or one electrons to complete a group of eight predominates.

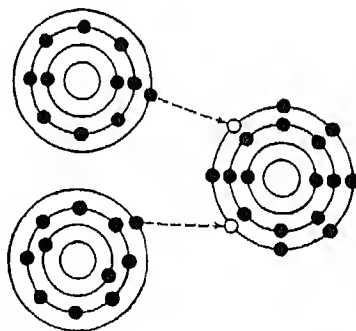


Figure 40 The Reaction of Two Atoms of Sodium with One Atom of Sulfur
Two electrons are transferred

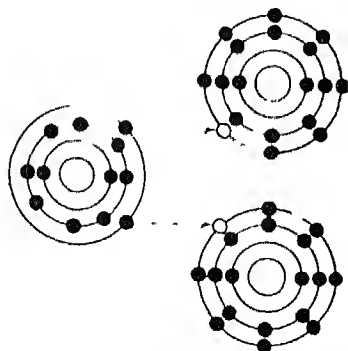


Figure 39 The Reaction of One Atom of Magnesium with Two Atoms of Chlorine

An atom that gains or loses electrons acquires an electrical charge. If one electron is removed from an atom in the manner described above, the atom will contain one more proton than the number of electrons remaining and, therefore, will have as a whole one unit of *positive* charge. The atom that acquires the electron will possess as a whole one unit of *negative* charge, because it will contain one more electron than the number of protons in its nucleus. The two charged particles resulting from the transfer of an electron from one atom to another will

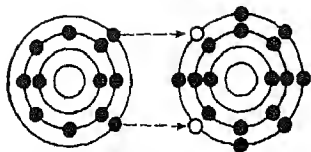


Figure 41. The Reaction of One Atom of Magnesium with One Atom of Sulfur

attract each other because of their unlike charges. This attraction explains one way in which the atoms of elements can be held together in compounds

The number of units of charge acquired by atoms as a result of electron-transfers depends upon the number of electrons that the atom loses or gains. For example, if an atom of element *A*, which can lose two electrons because it has only two in its outside level or group, reacts with atoms of element *B*, which contain seven electrons in the outside level, and which therefore can acquire only one more, the two electrons from one atom of *A* must go to two atoms of *B*. Thus an atom of *A* carrying two units of positive charge and two atoms of *B*, each carrying one unit of negative charge, result from the reaction. We can represent the compound that is formed as $A^{++}B_2^-$ or $(A^{++} + 2B^-)$ (see Figure 39)

10 Metals and Non-Metals

The atoms of the metallic elements tend to lose electrons when they react with other elements. They contain, in their outermost groups, usually only one, two, or three electrons, which are held rather weakly by the nucleus, it is relatively easy for other atoms that attract electrons more strongly to pull them off of the atom of a metal. Atoms of metals, therefore, take part in reactions in which they become positively charged. Atoms that remove electrons from others acquire negative charges. These are the atoms of non-metallic elements, such as oxygen, chlorine, bromine, and sulfur. The atoms of these elements must possess outermost electron-groups which are already well filled, and their nuclei must exert relatively

strong attraction for the electrons in even the outermost portions of the atoms

These concepts of atomic structure offer a reasonable basis for explaining the changes by which elements are converted into compounds, and the reason why two metals, such as sodium and calcium, or two non-metals, such as oxygen and chlorine, show no pronounced tendency to react with each other. The reaction of metals with non-metals, on the other hand, is explained more satisfactorily than Dalton's atomic theory could ever have explained it, atoms of metals give up electrons to atoms of non-metals, because the latter have stronger attraction for electrons. The concepts also explain why an atom of one element reacts with one atom of a second element, but with two of a third, and, perhaps, with three of a fourth.

11 Compounds Composed of Ions

Compounds produced in the manner we have just described, by the transfer of electrons from one atom to another, consist of electrically charged atoms. Such particles are called *ions*. In a crystal of a substance of this kind, e.g., sodium chloride, the ions (Na^+ and Cl^-) are arranged in a definite geometrical pattern (Figure 42) and are held together by forces resulting from the attraction of their unlike electrical charges. These forces are called electrostatic or *coulomb* forces. When sodium chloride dissolves in water, the ions separate and drift apart.

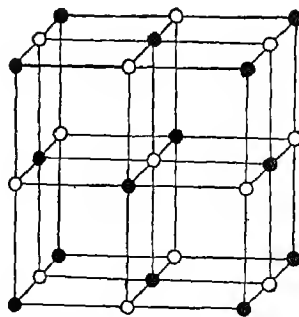


Figure 42. The Structure of a Crystal of Sodium Chloride
White circles represent sodium ions, black circles represent chloride ions

Neither in the crystal nor in solution are there any molecules of this substance or of any other substance composed of ions. In some compounds of this type, one (or perhaps both) of the ions is composed of a group of atoms. This is true, for example, of the sulfate ion, SO_4^{2-} , the nitrate ion, NO_3^- , the ammonium ion, NH_4^+ , and the carbonate ion, CO_3^{2-} . The letters used in these statements represent the elements, and the numbers (subscripts) show the number of atoms of each element in the ion. The signs (+, -, or =) indicate the number of units of electrical charge carried by the ion, the + sign represents one electron lost, the - sign, one electron gained, and the = sign, two electrons gained.

Compounds belonging to this group of substances are, for the most part, compounds consisting of the positive ion of a metal (or a positively charged group such as NH_4^+) and a negative ion made up of one or more non-metals. These substances may be classified as ionic compounds, because they are composed of ions.

12. A Typical Ionic Compound

Sodium chloride, common salt, is a good example of a compound composed of ions (see Figure 42). It contains the positively charged ion of sodium, Na^+ , and the negatively charged non-metallic ion of chlorine, Cl^- . For many years, chemists represented the composition of this substance by NaCl , as this expression indicates, it was formerly thought that sodium chloride was made up of molecules, each molecule containing one atom each of sodium and chlorine. But in view of what we know about ionic compounds, it would be better to indicate the composition of this substance as $\text{Na}^+ + \text{Cl}^-$. This expression does not mean that the two ions are joined together as a molecule, it means that in every crystal of salt, and in melted salt or in a solution as well, there is present *one sodium ion for each chloride ion*. In other words, when sodium and chlorine

form sodium chloride, equal numbers of the two kinds of atoms react.

13. Compounds Not Composed of Ions

Elements sometimes react in such a way that electrons are not transferred from one atom to another. Let us consider, for example, the combination of carbon and hydrogen. These elements form many compounds, of which the simplest is CH_4 . This substance does not contain any ions, and the atoms are actually held together in the form of a molecule containing one atom of carbon and four of hydrogen. Now each hydrogen atom has a single electron, and the carbon atom has four in its outer group. In forming the molecule, each atom *shares its electrons* with another (see Figure 43). This gives the carbon atom eight electrons in its outer group, and each hydrogen atom two, but neither atom really gains or loses any, hence the atoms are not electrically charged. Many compounds composed of two non-metals are produced by the sharing of electrons between atoms. In like manner, two or more atoms of the same element may combine to form molecules of the element. Thus, two atoms of hydrogen combine to make a molecule $\text{H} + \text{H} \longrightarrow \text{H}_2$. Compounds in which atoms share electrons may be called *molecular compounds*, since they are composed of molecules instead of ions. They are also called *covalent compounds*.

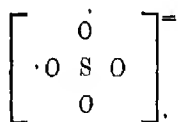
How are electrons shared and how does this arrangement hold atoms together? A reasonable, although purely hypothetical, answer can be suggested. The two electrons that form a pair probably move around both nuclei. If one could determine the time that they spend in different positions in the space near the two nuclei, one would probably find that most of the time is spent in the region that lies between the nuclei of the two atoms. This condition results, therefore, in the production of a region of relatively strong negative charge that attracts both positively charged nuclei and holds them together, since it lies between them.

There is, as yet, no complete explanation con-

cerning how or why two electrons team together to form a stable pair. It appears, however, that the two electrons that form such a pair spin upon their axes in opposite directions. Each electron thus sets up an electromagnetic field that attracts and holds the other.

Some of the compounds belonging to this class of substances are (1) many of the oxides, (2) compounds of two non-metals (CH_4 , CS_2 , NH_3 , etc.), and (3) compounds containing hydrogen in combination with one or more non-metals (HCl , H_2CO_3 , etc.). When some of these substances dissolve in water, or in certain other solvents, they may react with the water to produce ions, but in their pure state all of them are composed of molecules instead of ions. In the ammonia molecule two electrons are not shared, and in the water molecule four electrons (two pairs) of the electrons belonging to the oxygen atom are not used in binding oxygen to hydrogen.

Some ions contain two or more atoms (page 57). In these ions the atoms share electrons. The structure of the sulfate, SO_4^{2-} , ion, for example is



The four oxygen atoms of this ion have, normally, 6 electrons each in their outermost group (Figure 26). The sulfur atom (Figure 34) also contains 6 electrons in its outermost group.

Thus all the atoms of the ion together have 30 electrons, but 32 are required for the structure of the ion. These two additional electrons must, therefore, be removed from other atoms. They are responsible for the two units of charge that the ion possesses.

14 Valence Numbers and Valence Electrons

The valence of an element refers to the combining capacity of its atoms. It is expressed by a number that indicates the number of atoms of hydrogen with which one atom combines, or the number of atoms of hydrogen that one atom replaces in a compound. Thus, in water, H_2O , the valence number of oxygen is 2, because one atom of oxygen is combined with two atoms of hydrogen. In calcium oxide, CaO , the valence number of calcium is 2, because one atom of calcium is combined with one atom of oxygen and therefore must have the same combining capacity as two atoms of hydrogen, or twice as much as one atom of hydrogen.

The valence number of an element depends upon the number of electrons that an atom of the element gains, loses, or shares when it reacts with other atoms. In sodium chloride, NaCl , the sodium atom loses one electron, and the chlorine atom gains one. Therefore, the valence number of each element is 1. To indicate the difference — one atom gains and the other loses an electron — we frequently refer to the valence number of sodium as +1 and to that of chlorine as -1. In calcium chloride, CaCl_2 ,

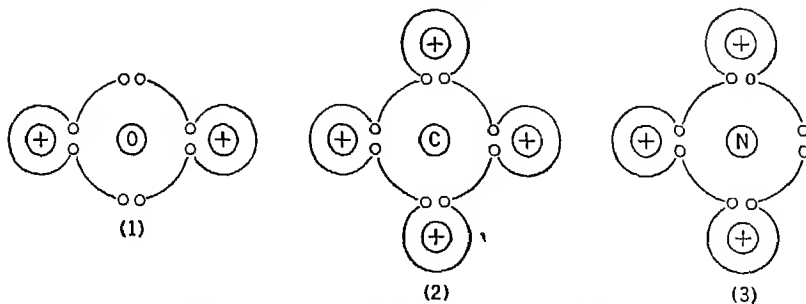


Figure 43. Compounds Formed by Atoms that Share Electrons

(1) Water; (2) Methane, CH_4 ; (3) Ammonia, NH_3 . When we write CH_4 , we mean that one molecule contains one carbon and four hydrogen atoms.

the valence number of calcium is + 2, and that of aluminum in $AlCl_3$ is + 3. In water, H_2O , the valence number of oxygen is 2, because the atom of this element *shares* electrons with two atoms of hydrogen. The valence number of hydrogen is one, because each atom shares one pair of electrons with oxygen. In carbon tetrachloride, CCl_4 , one carbon atom shares a pair of electrons with each of four chlorine atoms, therefore, carbon's valence number is 4. In carbon dioxide the carbon atom shares two pairs of electrons with each of the two oxygen atoms, and so here, too, carbon's valence number is 4. Because carbon has weaker attraction for electrons than chlorine, we frequently refer to the valence number of carbon (in carbon tetrachloride) as + 4 and that of chlorine as - 1. Likewise, oxygen has a negative valence number (- 2) in water and in carbon dioxide, because oxygen has a stronger attraction for electrons than carbon and hydrogen. For example, oxygen and chlorine do, in many of their compounds, remove electrons from certain atoms. Carbon rarely does so and, therefore, must have relatively weak attraction for electrons as compared to oxygen and chlorine. In only a few compounds does hydrogen gain electrons, consequently, its attraction must also be rather weak. In general, we may say that, in a compound of two elements that are combined by atoms sharing electrons, the element whose atoms contain the larger numbers of electrons in the outermost group has a negative valence number. Thus, in CCl_4 , the chlorine atom contains seven and the carbon atom four electrons in this group, and hence, the valence number of carbon is positive and that of chlorine is negative.

Since it has not gained, lost, or shared any electrons, we regard the atom of a free element as having a valence number of 0.

The electrons in the outermost group of an atom are the ones that are involved in reactions. Since they determine the combining capacity of the atom, they are sometimes spoken of as the *valence electrons* of the

atom, and the group to which they belong is called the valence group, or valence shell. Thus, the atom of magnesium (Figure 30) contains two valence electrons, and the atom of nitrogen (Figure 25) contains five.

Review Exercises

1. What are the kinds of particles of which atoms are composed?
2. What is the general plan upon which the structures of atoms are thought to be based?
3. What is the relation of a proton to a hydrogen atom?
4. Explain or define electron, atomic nucleus, nuclear charge.
5. Enumerate some of the ways in which the modern theory of the atom is more satisfactory than Dalton's theory.
6. In what way do the structures of atoms of metals differ from those of non-metallic elements?
7. What is an ion? How does it acquire its electrical charge?
8. To what does the term *atomic number* of an element refer?
9. What is the structure of an atom of an element that has an atomic weight of 19 and an atomic number of 9? Is it a metal or a non-metal?
10. The atom of aluminum contains 13 electrons. How many protons does it contain in its nucleus? If the atomic weight of aluminum is 27, how many neutrons does the nucleus of the atom contain?
11. With how many atoms of chlorine does one atom of aluminum react?
12. What is the valence number of aluminum? The atomic number? The mass number?
13. According to our modern theory of the atom's structure, upon what factor does the atomic weight of an element depend?
14. What conditions determine the maximum number of electrons that the atom of an element loses or gains in a reaction?
15. In what other way do atoms react to form compounds besides losing or gaining electrons?
16. The atomic number of an element is 16. How many groups or levels of electrons does an

atom of the element contain? Is this element one that will react with atoms of metals to form ionic compounds? Explain

- 17 Why do we represent the composition of salt, or sodium chloride, as $(\text{Na}^+ + \text{Cl}^-)$ and that of water as H_2O ?
- 18 What information is stated when we write the formula of a compound?
19. In what way is a chemical equation different from a mathematical equation?
- 20 What are isotopes? How are the structures of isotopes alike and how are they different?
21. In hydrogen chloride, HCl , one atom of hydrogen combines by sharing electrons with one atom of chlorine, in hydrogen sulfide, H_2S , two atoms of hydrogen combine with one atom of sulfur, in ammonia, NH_3 , three hydrogen atoms are combined with one of nitrogen, and in methane, CH_4 , four hydrogen atoms are combined with one carbon atom. Explain the fact that different numbers of hydrogen atoms react with one atom of chlorine, sulfur, nitrogen, and carbon
- 22 Of the atoms shown in Figures 29-37, page 53, which would be likely to lose electrons in

forming compounds, which would gain electrons, and which would not be likely to react at all?

- 23 There are three isotopes of hydrogen. The relative masses of their atoms as compared to 16 for the oxygen atom are approximately 1, 2, and 3, respectively. How do the structures of their atoms differ? In what ways are they identical?
- 24 Of the two kinds of atoms, nitrogen and magnesium (Figures 25 and 30 pages 52 and 53) which would you expect to form covalent rather than ionic compounds?

References for Further Reading

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- Latimer, W. M., and J. H. Hildebrand, *Reference Book of Inorganic Chemistry*, 2d ed., New York: The Macmillan Company, 1940
- Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*, New York: The American Book Company, 1936
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OXYGEN

The quantity of air which even a small flame requires to keep it burning is prodigious. It is generally said that an ordinary candle consumes, as it is called, about a gallon a minute. Considering this amazing consumption of air by fires of all kinds, volcanoes, etc., it becomes a great object of philosophical enquiry to ascertain what change is made in the constitution of air by flames and to discover what provision there is in nature for remedying the injury which the atmosphere receives by this means

PRIESTLEY

1. Introduction

The first element that we are to study at some length is the most abundant and, although invisible, one of the most familiar of all the elements. Oxygen and its compounds have many important functions in the life of all organisms and in the changes that occur in their environment. For animals it is the vitally necessary substance in the air that they breathe. Plants must have it to build the cellulose skeletons of their structures and to make the starch, sugar, fat, and protein that they require as foods. The oxygen of the air causes iron to rust, wood to decay, paints to harden, and coal to burn. These are but a few examples of the many natural processes that go on around us and that involve chemical changes for which oxygen is essential. The water that we drink and which is responsible for a large portion of the weight of our bodies is eight-ninths oxygen. Combined with other elements, oxygen is present in all our foods. The combustion of fuels to heat our houses, to cook our food, and to generate the energy required in industry is a chemical change in which one of the reacting substances is oxygen. It would be difficult to name another element that could be eliminated from our lives with more tragic and disastrous consequences.

The study of any element follows a general outline: (1) the occurrence and general importance of the element and its compounds; (2) the history of the element; (3) the methods of producing the element—both laboratory and industrial; (4) its physical and chemical properties; and (5) its uses.

In this chapter, chemical equations are used for the first time. Statements of the reactions are also given in words, and these are more important, at the present time, than the equations. One's ability to use equations, however, must be developed by experience in using them; hence, the more familiar you become with the equations in this chapter, the easier to understand will be your next experience with them.

One of the first important problems studied by chemists was the nature of the chemical change that occurs in burning, in the rusting of metals, and in the action of oxygen in the body. This question is one of the principal topics to be considered in this chapter and the next.

HISTORY OF OXYGEN AND COMBUSTION

Although it is the most abundant of all the elements, many others were known long before oxygen was discovered. Its properties,

and even the fact that it is an element, have been known only since about the time of the American Revolution. Its discovery was closely connected with the search for a satisfactory explanation of combustion.

2. The Phlogiston Theory of Combustion

As long ago as A.D. 700, the Chinese appear to have known that air contains an active and also an inactive substance. Mayow, in 1669, explained combustion and respiration upon the basis that air contains some gas that is active in promoting these processes. In the same year, however, Becher announced a theory that was designed to explain combustion as a change in which air played no fundamental part. In 1702, Stahl renewed and extended Becher's theory. According to the opinions of these men, combustible substances contain "phlogiston," which is liberated when the substances burn. In support of this view, it was said that the heat and light produced during combustion are caused by the escaping phlogiston. It was further pointed out that the residue left after burning often weighs less than the unburned substance. This observation, while not always true, was interpreted as meaning that something necessarily escapes when a substance burns. It was realized, of course, that the residues remaining after the combustion of some materials weighed more than the substances that were burned. This fact called for a change in the original phlogiston theory, and it was then that phlogiston became identified as the "principle of levity or lightness." Naturally, it was thought, if the levity of a body is removed during combustion, the product should weigh more than the body before it was burned. This view was inconsistent with the fact that burning — the escape of phlogiston — sometimes left a residue that weighed less than the original substance. Furthermore, the theory offered no satisfactory explanation of the important rôle that air plays in combustion.

The rôle of the air could not be overlooked entirely even by the phlogistonists, for they

were obliged to recognize that the presence of air was necessary for the occurrence of combustion. The action of the air was explained by saying that it absorbs phlogiston, and that if air is not present, of course, the phlogiston remains in the substance.

The phlogiston theory, however, was not so entirely unreasonable as it sounds today. To men who looked upon the problem without our knowledge of oxygen and its properties, fire appeared to destroy. A large portion of the burning body appeared to escape into the air. The fact that invisible gases, such as carbon dioxide, are produced, and that these mingle with the air about the body, was not known in the days when the phlogiston theory was accepted. Combustion appeared to be a decomposition, during which some essential constituent of substances escaped into the air, leaving behind a small mass of ash, which was then called *calx*. This explanation of the mystery of burning and of fire was perhaps the most reasonable one that could be formulated in the seventeenth century. Even when more facts than were then known had been accumulated, this solution of the problem had to be eliminated before the correct solution could be presented and accepted. The phlogiston theory served as a guide to studies of the air and of combustion throughout most of the eighteenth century, and not until the latter part of that century did observations made by Priestley and Scheele lead finally to a better understanding of combustion and its dependence upon what we now know is the oxygen of the air.

3. The Discovery of Oxygen

Priestley is usually credited with the discovery of oxygen. He was interested in the gases that are liberated when different substances are heated. Priestley did not regard these gases as essentially different substances, but thought of them as different kinds of air. The method that he used to heat the substances from which the gases were expelled is interesting. A tube, closed

at one end, was filled with mercury and inverted in a dish or trough filled with the same liquid. The substance to be heated was introduced and made to float upon the surface of the mercury in the upper part of the tube. Here it was heated by converging upon it the rays of the sun by means of a lens. One of the substances that Priestley heated in this manner was mercuric oxide. In the gas that was liberated by heating this substance, a candle burned much more brilliantly and vigorously than in ordinary air. In preparing this gas, Priestley had discovered oxygen, but he did not recognize the discovery. He explained the properties of the gas by saying that it was "dephlogisticated air." In 1775, he wrote to the Royal Society concerning his discovery as follows:

But the most remarkable of all the kinds of air that I have produced by this process is one that is 5 or 6 times better than common air for the purpose of respiration, inflammation, and, I believe, every other use of common atmospherical air. As I think I have sufficiently proved that the fitness of air for respiration depends upon its capacity to receive the phlogiston exhaled from

the lungs, this species may not improperly be called dephlogisticated air.

Air in which phlogiston is absent should be a better absorber of phlogiston, of course, than air that is saturated or even air that contains some phlogiston but not as much as it can absorb. Priestley was an ardent follower of the phlogiston view to the end of his life in 1801. His views are expressed in the following quotation, which also serves to show the extent of his experiments and the range of his imagination:

From the greater strength and vivacity of the flame of a candle in this pure air it may be conjectured that it might be peculiarly salutary to the lungs in certain morbid cases, when the common air would not be sufficient to carry off the phlogistic putrid effluvia fast enough. But we may also infer from these experiments that though pure dephlogisticated air ought to be very useful in medicine, it might not be so proper for us in the usual healthy state of the body; for, as a candle burns out much faster in dephlogisticated air than in common air, so we might, as may be said, live out too fast, and the animal power be too soon exhausted in this pure kind of air. A moralist, at least, may say that the air which nature has provided for us is as good as we deserve. After having ascertained the superior goodness of dephlogisticated air I have gratified the curiosity (to taste it myself) by breathing it. The feeling of it to my lungs was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that, in time, this pure air may become a fashionable article in luxury. Hitherto only two mice and myself have had the privilege of breathing it.

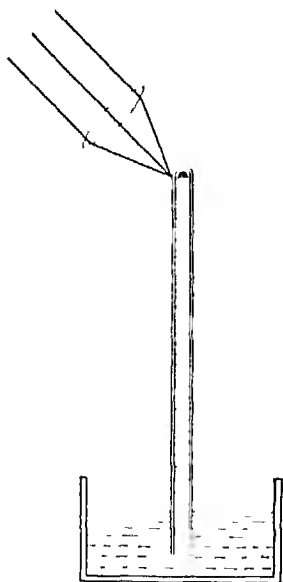


Figure 44 The Apparatus Used by Priestley in the Experiments by Which He Discovered Oxygen

Scheele prepared the same gas from several substances in 1771. Furthermore, he understood that it was present in the air, that it combines with many substances, and that some of the compounds thus formed decompose upon heating to liberate the same gas again. Although Scheele's discovery really predates Priestley's, the latter is usually given the credit for discovering oxygen, since Scheele's results were not published until 1777. In the meantime Priestley's discovery

had been recognized as one of far-reaching significance

4. Lavoisier's Experiments and the Recognition of Oxygen as an Element

Priestley's "dephlogisticated" air came to the notice of Lavoisier, who was, in our opinion, the outstanding chemist of the eighteenth century. Lavoisier saw in Priestley's results the probable solution of the problem of combustion. He reasoned that if a candle burns more brilliantly in the gas evolved when mercuric oxide is heated, than in air, then this gas contains in a concentrated condition the component of air that causes substances to burn. He believed that this active component of air combines with substances during combustion. According to this point of view, therefore, an increase in weight should be expected when one compares the weight of the products with those of the materials that burn.

To prove this point, or rather to determine whether or not this explanation of combustion was more sound than the phlogiston theory, Lavoisier heated mercury in a retort with air (Figure 45) for twelve days. The neck of the retort extended through water in a trough and into a bell-jar, which was filled with air and inverted in the trough. It was found that the volume of air in the bell-jar and retort decreased by an amount equal to one fifth of the original volume, and that the surface of the mercury became covered with a layer of a red powder. The gas left in the bell-jar did not possess the properties of air, it did not support combustion and it did not

sustain life. Furthermore, Lavoisier found that when the red powder that formed on the surface of the mercury was heated, it liberated a volume of gas equal to the volume of air that had disappeared when it was made. At the same time mercury was formed. The gas that was liberated possessed the properties lost by the sample of air during the heating of the mercury, but these properties were much more strongly manifested than in air. It was strongly indicated, therefore, that in addition to this active gas, which is evidently present in the air, there is another component that is inactive. Thus Lavoisier showed that air is a mixture, one part of which combines with metals when they rust, supports combustion, and is necessary for life. There could no longer be any doubt that Priestley's "dephlogisticated air" was the same substance as this active component of air, which Lavoisier recognized as an element. The phlogiston theory was overthrown.

Because he thought that all acids must contain this element, Lavoisier gave it the name of *oxygen*, which means "acid former." This view of acids is erroneous, but the term has been retained as the name of the element. Lavoisier called the inactive component of the air *azote*. We now call it *nitrogen*.

OCCURRENCE AND PRODUCTION

5. Occurrence

About one half of the earth's crust, including the atmosphere, consists of oxygen. Approximately 60 per cent of the weight of our bodies is oxygen. This element is responsible for about 50 per cent of the material in common rocks, and cellulose, the woody portion of plants, contains about the same percentage. It occurs in the air in the free state. In combinations with other elements it is found in all rocks, in soil, in many ores and minerals, in all food products, and in cotton, wool, wood, and many other natural and synthetic materials. The total weight of all the oxygen in the earth's crust, which

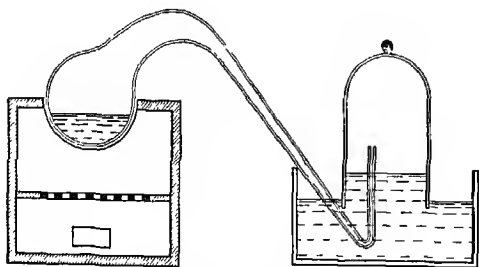
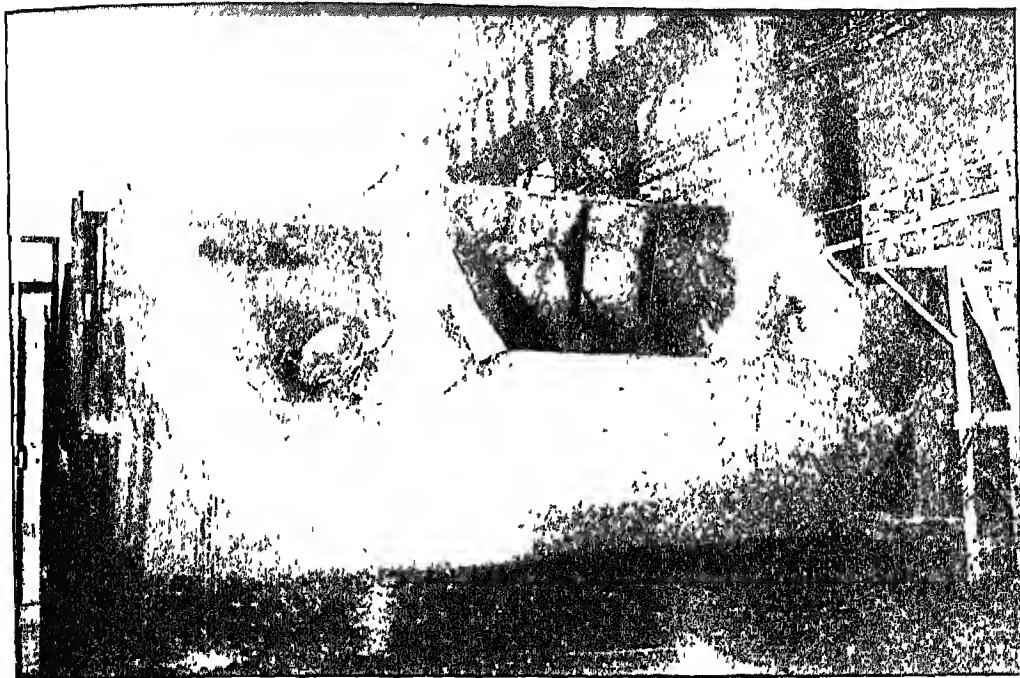


Figure 45 Lavoisier's Apparatus



Courtesy of Air Reduction Sales Company

Figure 46 Welding Operations on a Locomotive Tender

meludes that in soils and rocks, in water, in air, and in the bodies of all plants and animals, is about the same as the weight of all the other elements together

6. Production General Statement

Since oxygen occurs in air and in water, we should expect to find that the industrial supply of this element is obtained from these sources. Oxygen is in the uncombined state in air, hence, to produce it from this source no chemical change is necessary, but it must be separated from other substances that are always present. Water must be decomposed when it is used as a source of oxygen. This process requires energy and special methods of using energy; simple heating in a vessel will not decompose water except when it is heated to temperatures that are not industrially practical. Even if water could be decomposed by heat, the separation of oxygen from the hydrogen liberated at the same time would offer considerable difficulty. For

these reasons, water is decomposed into its elements by the use of electrical energy. The production of oxygen from air also requires energy but, in general, this process is more practical than production from water.

7. Preparation of Oxygen from the Air

When air is compressed and cooled to a temperature of about -200°C , it can be converted into a liquid. Cooling to this extremely low temperature is accomplished by allowing highly compressed air to expand through a small valve (Figure 17) into a chamber where the pressure is lower. To expand, a gas must absorb heat, and in this case the heat must come from the coil that carries the compressed air, since the apparatus is thoroughly insulated to prevent the absorption of heat from the outside. The air that escapes from the valve at the end of the coil is returned to the compressor, where it is again subjected to a high pressure. It is then passed through coils in a cold mixture

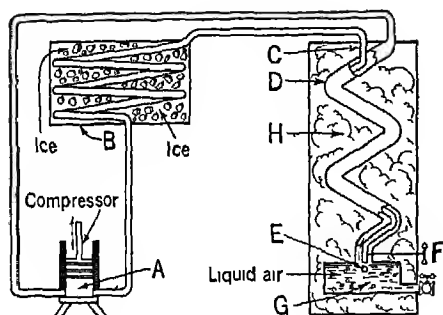


Figure 47 The Liquefaction of Air

A, compressor; B, cooling coils, C, pipe carrying compressed air; D, pipe carrying cold air back to compressor, E, expansion valve, F, valve handle; G, liquid air, H, insulation.

of ice and salt to remove the heat resulting from the compression, and finally, it is allowed to expand again. In this way the air that escapes through the valve is reduced to a gradually decreasing temperature, until at last it is sufficiently cooled to become a liquid.

Liquid air is a mixture, like air itself, of all the components of the atmosphere except water vapor and carbon dioxide, which liquefy at a much higher temperature than oxygen and nitrogen and which, therefore, can be removed before the liquefaction of the main portion of the air occurs. If liquid air is allowed to evaporate, the different substances that it contains escape at different temperatures. Approximately four fifths of the air is nitrogen, the inactive component, which boils at -195.8° . Oxygen boils at -183° . Hence nitrogen boils away first, leaving a residue that is almost pure oxygen. The oxygen is then allowed to evaporate and the gas is compressed in steel cylinders. Within these cylinders the pressure is one thousand pounds or more per square inch.

8. Preparation of Oxygen from Water

Water can be decomposed into oxygen and hydrogen by means of a direct current of electricity. Since pure water does not conduct the current, a small amount of sodium hydroxide or sulfuric acid is added to make a solution that will serve as a conductor. Oxygen collects at the positive terminal of

the cell (Figure 48), and hydrogen collects at the negative terminal. This reaction, called the *electrolysis* of water, is a type of chemical decomposition in which electrical energy, instead of heat, is used to bring about the decomposition of water. As a cell is operated, the sodium hydroxide or sulfuric acid is not consumed. Water alone is added to replace that which is converted into oxygen and hydrogen. The two gases are collected in separate containers and are therefore obtained in a fairly pure state. This method of producing oxygen is profitable when there is a good market for both hydrogen and oxygen, though in general it is not as extensively used as the method of producing oxygen from liquid air.

9. Preparation of Oxygen from Certain Substances that Decompose when Heated

When small quantities of oxygen are desired in the laboratory, certain substances that contain oxygen can be decomposed partially or completely by heating. We have

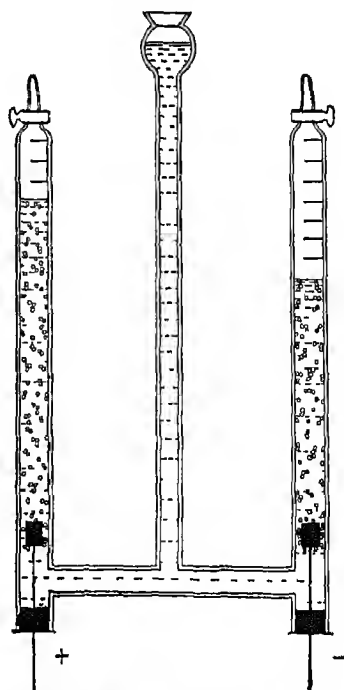
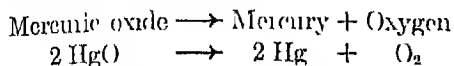
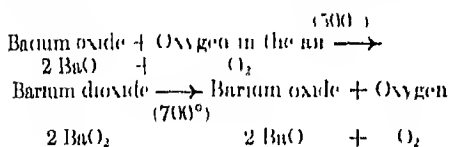


Figure 48 The Electrolysis of Water

already noted that Priestley prepared the element by heating the substance that we call mercuric oxide. This substance contains 7.385 per cent of oxygen.

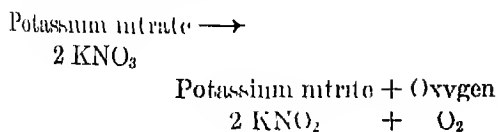


But this method of preparing oxygen is not one that can be applied generally to all oxides or even to the oxides of all metals. The oxides of calcium and magnesium (CaO and MgO), for example, resist all attempts to decompose them by heat, although they would probably decompose if a sufficiently high temperature could be attained. On the other hand, the oxides of the least active metals, such as gold and silver, decompose on heating. This is also true of the oxides of chlorine, which decompose with explosive violence if warmed only slightly. Other oxides that yield a portion of the oxygen that they contain when they are heated include barium peroxide, BaO_2 , and red lead, Pb_3O_4 . If barium oxide, BaO , is heated with air at 500° , barium peroxide is formed. When the pressure is reduced and the temperature is raised to 700° , barium peroxide decomposes, forming barium oxide and oxygen.



This is Bunsen's process, which was used to some extent at one time to obtain pure oxygen from the air. Not all the oxygen contained in barium peroxide is liberated. Barium oxide contains 10.13 per cent of oxygen, and barium peroxide contains 18.89 per cent.

If potassium or sodium nitrate is heated, some oxygen is liberated, and the nitrite of the metal is formed.

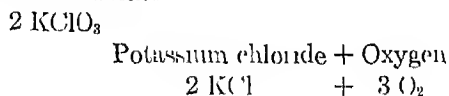


It will be noted that only one third of the total oxygen content of the potassium nitrate is liberated in this reaction. Potassium nitrate contains 47.57 per cent of oxygen, and sodium nitrate contains 56.47 per cent.

10. Preparation of Oxygen from Potassium Chlorate

Potassium chlorate contains 31.9 per cent of potassium, 39.2 per cent of oxygen, and 28.9 per cent of chlorine. It decomposes when it is heated to a temperature above its melting point (368°C).

Potassium chlorate \longrightarrow



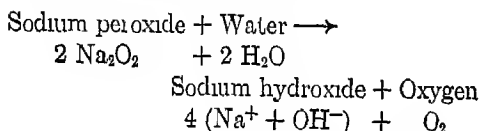
Oxygen is liberated, and there is left a white solid, which is a compound of potassium and chlorine. This is potassium chloride, KCl . The reaction goes on at noticeable speed only when a moderately high temperature is reached, although there appears to be no one temperature at which it begins. At temperatures below the melting point of potassium chlorate, oxygen may be liberated, but the speed of the reaction is so slow that it is not noticeable. If a little manganese dioxide, MnO_2 , is mixed with the potassium chlorate and the mixture is heated, oxygen is liberated readily at a temperature (200°) considerably below the melting point of potassium chlorate. The oxygen does not come from the manganese dioxide, since this substance does not decompose at this temperature. Furthermore, after the reaction is completed, it is possible to separate the manganese dioxide from the potassium chloride in the residue by taking advantage of the fact that the latter is very soluble in water while the former is not. The quantity of manganese dioxide recovered in this manner is equal to the amount originally added. We therefore conclude that manganese dioxide only increases the speed of the decomposition of potassium chlorate at relatively low temperatures and is not itself consumed during

the reaction. A substance that influences the speed of the reactions of other substances without undergoing any permanent chemical change is called a *catalyst*. We say, therefore, that manganese dioxide catalyzes the decomposition of potassium chlorate.

The usual method of preparing and collecting samples of oxygen from potassium chlorate is shown in Figure 49. Since oxygen is only slightly soluble in water, it is collected by the displacement of water in a bottle which has been filled with water and placed in an inverted position on a shelf of the trough.

11. Preparation of Oxygen from Sodium Peroxide

When sodium peroxide, Na_2O_2 , is placed in water, or water is poured over it, oxygen is evolved and the following reaction occurs:



This reaction proceeds very slowly if the water is cold, but if the water is hot it occurs with explosive violence. The reaction can also be made to occur at a lower temperature with increased speed, if a catalyst such as cupric oxide, CuO , is added.

12. A Note on the Equations Used Above

In discussing the preparation of oxygen from different compounds, we have used equations for the first time to express chemical facts. A few

remarks concerning these equations may be appropriate at this time.

In the first of these equations — that dealing with mercuric oxide — the formula of this substance is written as HgO to indicate that it contains one atom of mercury for each atom of oxygen. Likewise, the formulas KClO_3 , KCl , KNO_3 , KNO_2 , Na_2O_2 , and NaOH show the relative numbers of atoms of the different elements that compose these compounds. Thus, in potassium chlorate there are three atoms of oxygen and one of chlorine for each atom of potassium. The number 2 written before the formula HgO indicates that twice as much of this substance as is indicated by the formula must be used to balance the equation. We also place the number 2 before the symbol of mercury (2Hg), because two atoms of this element are liberated when we use 2HgO . We do not write these atoms as Hg_2 , because there are not two atoms of mercury in a molecule. It is necessary to write 2HgO on the left-hand side of the equation, because two atoms of oxygen must be liberated, these are required to form one molecule, O_2 , of oxygen, which is the smallest quantity of this substance that can exist in the free state. Similar explanations will account for the numbers of molecules or atoms of the different substances indicated in the other equations.

PROPERTIES

In general chemistry it is important that the student should have a record of the physical and chemical properties of the elements, and the text should supply this information. It is not intended that detailed facts, such as densities, boiling points, and freezing points, should be memorized. Such

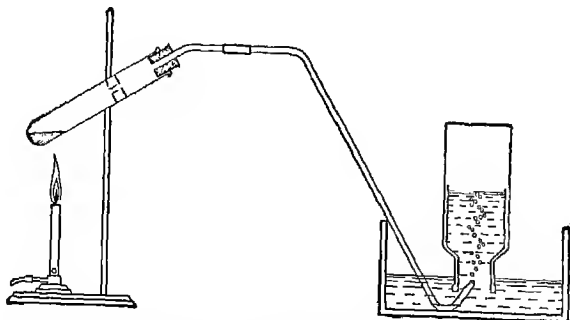


Figure 49 The Preparation of Oxygen from Potassium Chlorate

information is given in the text so that it will be available when it is needed. The student should become acquainted with the important physical features and with the behavior of the elements, as, for example, the state of the substance under ordinary conditions, solubility in water as compared with other substances, relative ease with which the substance can be liquefied, if it is a gas, or the ease with which it can be vaporized, if it is a liquid, and so on. Among the important chemical properties of an element are (1) the kinds of elements (and, sometimes, compounds) with which it reacts, and (2) the types of compounds that it forms with them.

13. Physical Properties

Oxygen exists naturally as a gas, but the liquid and solid states can be prepared at low temperatures. Gaseous oxygen is 1.105 times as heavy as air. One liter (at 0°C and at the average atmospheric pressure at sea-level) weighs 1.429 g. It is colorless, tasteless, and odorless. In very thick layers it appears to be slightly blue in color. It can be liquefied at -118°C under a pressure of 50 atmospheres and at lower temperatures by applying the proper pressure. The gas cannot be liquefied at any pressure when the temperature is above -118°C. Liquid oxygen is blue in color. At atmospheric pressure, it boils at -182.5°C. It is attracted by a magnet. Solid oxygen, a light blue, snow-like substance, can be produced by extraordinary cooling methods, such as cooling by the rapid evaporation of liquid hydrogen. The solid melts at -218.1°C.

Oxygen is only slightly soluble in water. At 20°C, and at atmospheric pressure, about 3 ml. of oxygen dissolves in 100 ml. of water. It is twice as soluble as nitrogen. Animals that live in water depend upon dissolved oxygen for their respiratory needs.

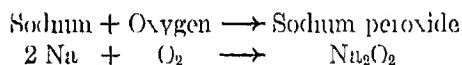
14. Chemical Properties

At low temperatures, oxygen is only moderately active, not many substances that

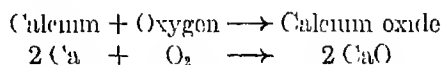
come into contact with it react to a noticeable degree at ordinary temperature. At higher temperatures, it combines directly with many of the elements — both metals and non-metals — to form oxides. It does not combine directly with chlorine, bromine, and iodine or with some of the least active metals, such as gold, silver, and platinum. And of course it does not combine with the inert gases. Oxides of some of the elements with which oxygen does not combine directly can be made indirectly from compounds of the elements which contain oxygen. Thus, nitrogen and oxygen do not combine, except at very high temperatures, to form nitric oxide (NO) or nitrogen dioxide (NO₂), but these two oxides are readily prepared from nitric acid (HNO₃) and from other compounds that contain a third element.

15. Reactions of Oxygen with Metals

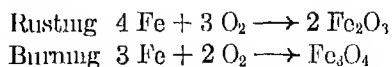
The most active metals, such as sodium and potassium, react readily with oxygen at low temperatures and burn brilliantly when heated in air or pure oxygen.



Calcium burns almost as brilliantly and vigorously.

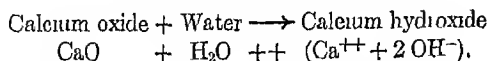
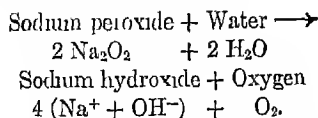


These active metals combine very vigorously with the oxygen in the air, although they burn even more vigorously, of course, in pure oxygen. Iron, which combines only very slowly with the oxygen in the air to form ferric oxide (iron rust), burns brightly in pure oxygen, if it is heated to the required initial temperature, forming magnetic iron oxide, Fe₃O₄.



Small iron wire or steel wool burns much more readily than heavier iron wire, iron screen, or nails.

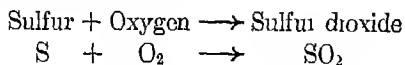
If the oxides of the metals are mixed with water, some of them dissolve readily. Others dissolve only slightly, or not at all, as far as ordinary means of observation permit one to judge. The solutions turn red litmus paper blue. This effect is the result of reactions of the oxides with water, forming *hydroxides* that act as *bases*. A solution of the hydroxide of an active metal in water has certain properties frequently designated by describing the solution as *alkaline*.



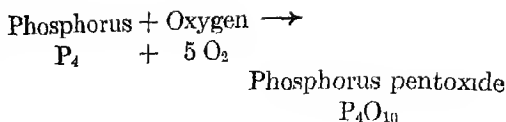
Each of the solutions which are formed when these reactions take place cause one's fingers to feel "soapy" when placed in the solutions and rubbed together. This property, and the effect of the solution upon *litmus*, are characteristics of solutions of hydroxides of the active metals. *Litmus* is an *indicator*, in an alkaline solution its color is blue, and in a solution of an acid, such as vinegar, it is red. There are many other substances that act as indicators, among these are *phenolphthalein* and *methyl orange*. The former is red in an alkaline solution and colorless in the solution of an acid. The latter is red in the presence of an acid, and yellow in an alkaline solution. The basic and alkaline properties of an aqueous solution of sodium or calcium hydroxide are really properties of the hydroxyl ion, OH^- .

16. Reactions of Oxygen with the Non-Metals

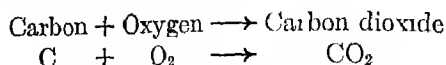
Many of the non-metals also combine with oxygen. Sulfur, if it is first heated in a flame until it ignites and is then placed in a vessel filled with oxygen, burns with a much more brilliant flame, and the reaction is much more vigorous, than in air.



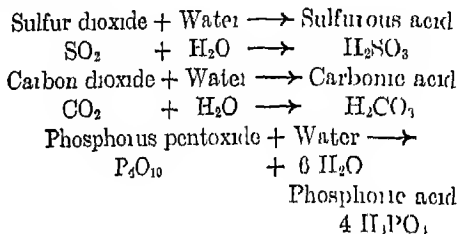
The oxide that is formed is called sulfur dioxide. Red phosphorus burns with a very brilliant flame, forming phosphorus pentoxide (P_4O_{10}), which appears as a dense white cloud of smoke.



If carbon in the form of charcoal is first heated to the point where it begins to burn, it continues to burn in pure oxygen and does so at a much faster rate than in air. Whenever carbon is completely burned, carbon dioxide (CO_2) is produced.



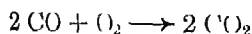
The oxides of the non-metals react with water to form acids.



The solutions formed when these oxides react with water show all the typical properties of acids. They turn blue litmus red and are sour to the taste. A more complete discussion of the properties and chemical nature of acids and bases will be given in Chapter 12.

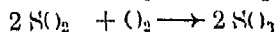
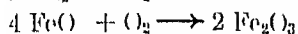
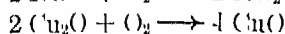
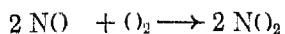
17. Reactions of Oxygen with Compounds

In addition to its direct combination with elements to form oxides, oxygen also reacts with many compounds, sometimes to form the oxides of the elements contained in the compounds, and sometimes to produce other kinds of compounds. Thus, carbon monoxide (CO) is converted into carbon dioxide (CO_2) when it burns in air or in pure oxygen.



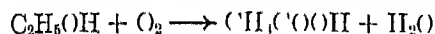
Similarly, many other oxides in which the proportion of oxygen to the other element is smaller than is possible are converted into "higher" oxides. The reactions of some of

these oxides are shown in the following equations



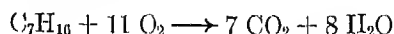
Some elements form only one oxide, for these, of course, further reaction with oxygen is out of the question. This is true of the oxide of aluminum, Al_2O_3 , and the oxide of calcium (lime), CaO .

Oxygen also reacts with many other substances that are not oxides. Vinegar is produced by a reaction of alcohol with oxygen in the presence of certain kinds of bacteria.

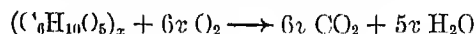


Vinegar is essentially a solution of acetic acid (CH_3COOH) in water. The linseed oil in

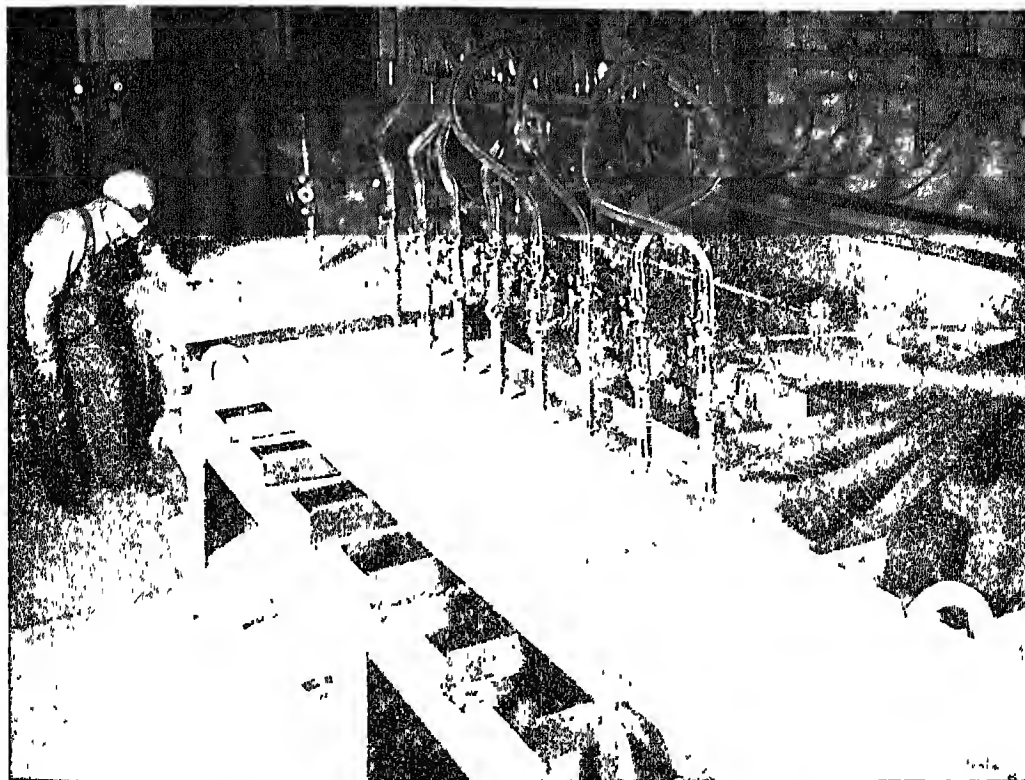
paint hardens because of a reaction of the oil with the oxygen in the air. Gasoline, which we may represent as heptane (C_7H_{16}), although it contains also a few other compounds of similar composition, burns to form carbon dioxide and water in the presence of an excess of oxygen or to form carbon monoxide and water in the presence of a limited supply of oxygen.



Paper, which is essentially cellulose, ($\text{C}_6\text{H}_{10}\text{O}_5$) $_x$, burns in an adequate supply of air to form carbon dioxide and water.



The formula of cellulose is represented as ($\text{C}_6\text{H}_{10}\text{O}_5$) $_x$ because the number of $\text{C}_6\text{H}_{10}\text{O}_5$ units that the molecule contains is unknown.



Courtesy of Air Reduction Sales Company

Figure 50 Eight Torches Mounted on a Bar Used for Cutting Purposes in a Multiflame Machine

18. Uses of Oxygen

The uses of oxygen in relation to life, in important reactions such as decay, the formation of oxides, and the hardening and drying of paints, and in the combustion of fuels to produce the energy that warms our homes and operates the machinery of industry, have been pointed out already. All of these uses, however, involve the oxygen of the air and do not require the pure substance. Pure oxygen also has many uses, and its production constitutes an industry of considerable proportions. About 2,500,000,000 cubic feet, valued in excess of \$20,000,000, is produced in the United States annually. Most of this (between 85 and 90 per cent) is produced by the fractional distillation of liquid air, and the remainder by the electrolysis of water.

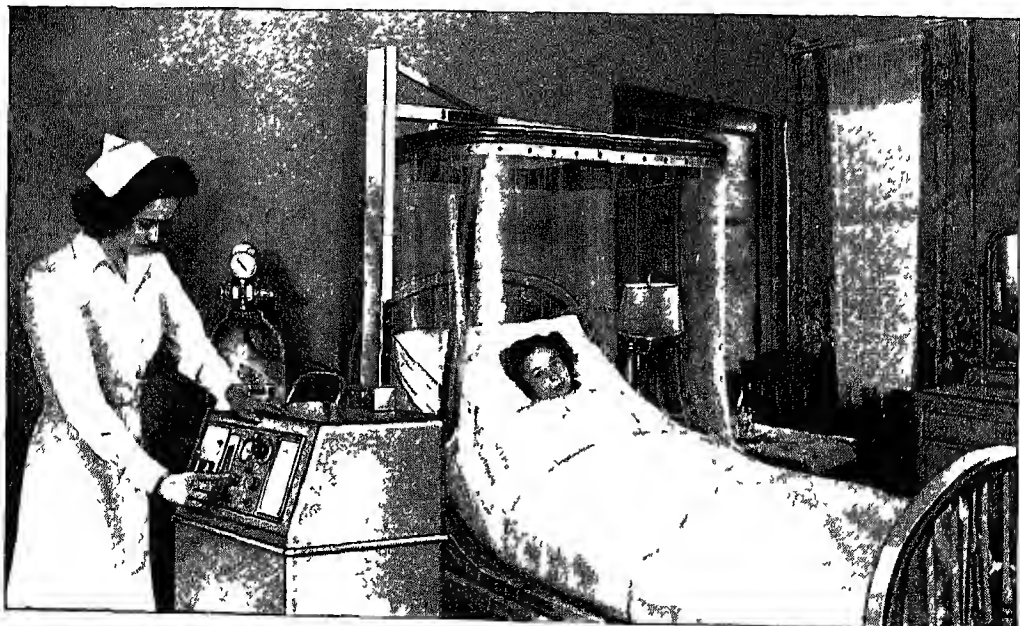
The oxygen tent is familiar equipment of almost all hospitals. Oxygen is used in the medical profession to aid in cases of impaired respiration, as in pneumonia. It may also be given to patients who have breathed poisonous gases and administered in conjunction with certain anaesthetics during operations.



Courtesy of Gulf Oil Corp.

Figure 51. Electric Arc Welding

This is a photograph of welding operations on the "Big Inch" pipeline, constructed during the war for the transportation of oil from Texas to New York and Philadelphia.



Courtesy of the Ohio Chemical and Manufacturing Company

Figure 52. An Oxygen Tent

Tanks of oxygen are carried in submarines to renew the oxygen in the air and may be used by aviators who fly at very high altitudes.

In industry, oxygen is used with acetylene in the oxyacetylene blowpipe for welding iron and steel during the construction of the steel framework of buildings, bridges, and so on. The oxygen-hydrogen blowpipe is used for cutting steel beams and plates when structures are demolished; the metal is heated to incandescence by the blowpipe, the hydrogen is then shut off, and oxygen alone is used to burn the metal. The heat that is liberated maintains the proper working temperature, and the metal can be cut by the flame almost as readily as a knife cuts a loaf of butter. Complicated structures that are of value only as scrap iron can thus be cut into smaller parts which can be transported more conveniently. Liquid oxygen may be mixed with carbon dust and oil to produce an explosive used in coal mining. This explosive has certain advantages over others, such as dynamite, for no injurious or obnoxious fumes are produced upon explosion, and cartridges which are not exploded are not likely to be dangerous, since the liquid oxygen soon evaporates. Future developments may lead to many other extensive uses of oxygen. Already some use is made of it, for example, in enriching the air that is used to burn out the impurities in iron during the manufacture of steel.

Review Exercises

1. Describe the contributions of Priestley, Scheele, and Lavoisier to the early history of oxygen.
2. Why did Priestley call the gas that he prepared "dephlogisticated air"?
3. How did the phlogiston theory differ from the modern explanation of combustion?
4. Name four compounds from which oxygen can be prepared and describe the method used in each case.
5. How does the presence of manganese dioxide influence the production of oxygen from po-

tassium chlorate? How could you show that it produces no oxygen itself during the reaction?

6. What weight of oxygen could be obtained from 1000 g of potassium chlorate? What volume would this weight of oxygen occupy? (The data required for this and other problems in this list will be found in this chapter. The density of oxygen, page 69, is the weight of a liter of the gas, measured at 0° and the average pressure of the atmosphere at sea level. This value varies with the temperature and pressure, but we shall not consider such variations at this time.)
7. A mixture consisting of 10 g of manganese dioxide and 50 g of potassium chlorate is heated until the liberation of oxygen is complete. What is the weight of the residue in the container? What is it?
8. Following the examples given on page 71, write equations for the combustion of the following substances (in the air): nonane, C_9H_{20} , methyl alcohol, CH_3OH , and acetone, C_3H_6O .
9. What difference between the metallic and the non-metallic elements has been described in this chapter?
10. Since oxygen combines with so many elements, how do you account for the large amount of it that remains uncombined in the atmosphere?
11. Calculate the weights of mercuric oxide, sodium nitrate, barium peroxide, and potassium chlorate required to produce 100 liters of oxygen measured at $0^{\circ}C$ and at the average sea level atmospheric pressure.
12. If mercuric oxide costs \$1.75 per pound, sodium nitrate \$0.20, barium peroxide \$0.38, and potassium chlorate \$0.25, which compound would be the cheapest source of oxygen for laboratory experiments?
13. What volume of oxygen will dissolve in one liter of water at $20^{\circ}C$? Approximately what percentage by weight of such a solution is (free) oxygen?
14. What volume of oxygen measured at $0^{\circ}C$ and at the average sea level pressure of the atmosphere can be produced by the electrolysis of 50 g of water?
15. If all the oxygen in 50 g of potassium chlorate is liberated and used to produce mercuric

oxide, what weight of the latter can be made?

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OXIDATION AND COMBUSTION; OZONE

It is one of the lessons of the history of science that each age steps on the shoulders of the ages that have gone before

SIR MICHAEL FOSTER

1. Introduction

This chapter is concerned with one major problem. The nature of the chemical change that we call combustion and other slower reactions of a similar nature. These reactions are important, for reasons already explained (preceding chapter). They constitute the chemical changes that all of us know best even before we begin the study of chemistry.

2. The Nature of Oxidation and Combustion

All of the reactions in which oxygen combines with free elements and those in which compounds react with oxygen may be included under the general term of *oxidation*, which includes, however, many other chemical changes. These changes may be slow or rapid, thus, iron is oxidized slowly when it rusts, and it is also oxidized when it burns rapidly and brilliantly in pure oxygen. When it burns, iron undergoes *combustion*.

Before we can properly define these terms, we must describe the many types of reactions to which they are applied. Oxidation and combustion are not terms that are applied only to the reactions of oxygen. They are much more general. If iron is exposed to the action of moist chlorine, it combines with that element to form ferrous chloride or ferric chloride, FeCl_2 or FeCl_3 . If heated and if finely enough divided, it may even *burn* in pure chlorine, forming the same compounds. Finely divided zinc and sulfur react vigorously to form zinc sulfide when heated. The reaction liberates heat and light and closely

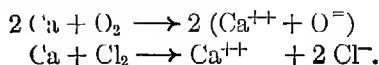
resembles, in every way, the burning of paper or wood in air or pure oxygen. A stream of hydrogen gas, when ignited, burns in chlorine to form hydrogen chloride, exactly as it burns in oxygen to form hydrogen oxide (water). These reactions involve oxidation just as truly as the combinations of iron and zinc with oxygen to form oxides.

In arriving at a proper definition for oxidation, we must note, also, that certain compounds in which an element is already combined with oxygen, or with some other non-metallic element such as chlorine or sulfur, may combine with more of the same element. Thus, carbon combines with oxygen, when the supply of the latter element is limited, to form carbon monoxide (CO). This substance may combine with more oxygen to form carbon dioxide (CO_2). Similarly, iron combines with chlorine to form ferrous chloride (FeCl_2), and in the presence of sufficient chlorine, this compound is converted into ferric chloride, FeCl_3 .

We must note, too, that the oxygen, chlorine, or other non-metal that takes part in the oxidation need not necessarily be in the free state, it may be already combined with other elements. For example, magnesium, if heated in the presence of steam, burns brilliantly. Here, the magnesium combines with the oxygen that was originally present in the water. It forms magnesium oxide (MgO), and the hydrogen of the water is set free.

3. A Definition of Oxidation

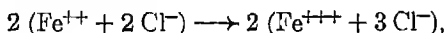
Each of the following reactions involves the oxidation of calcium.



In each of these reactions the same change occurs in the atoms of calcium, namely, the loss of two electrons per atom. In the first reaction the electrons are removed from calcium by oxygen and in the second by chlorine. In each reaction, therefore, the valence number of calcium is increased from 0 to +2. In the reaction of iron with chlorine,

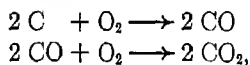


the iron atom loses two electrons to chlorine atoms, and the valence number of iron is increased from 0 to +2. When ferrous chloride, FeCl_2 , is converted into ferric chloride, FeCl_3 ,



another electron is lost by each atom of iron, and the valence number of iron is again increased, this time from +2 to +3.

When carbon reacts with oxygen to form carbon monoxide, and again when carbon monoxide is converted by additional oxygen into carbon dioxide,

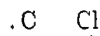


carbon is oxidized, although there is no transfer of electrons from one atom to another, and no ions are formed. The valence number of carbon, however, does increase first from 0 to +2 and then to +4.

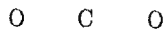
*We may define oxidation as a reaction in which the positive valence number of some element is increased or the negative valence number is decreased.*¹ If the compound produced is ionic in character, we may add that oxidation involves the loss of electrons by an atom or an ion.

Perhaps we should add a few words regarding oxidation in those reactions in which electrons

are only shared by atoms. In such cases, the assignment of positive and negative valence numbers to elements is largely arbitrary. Even when atoms share electrons, however, there is usually considerable difference in the degree of attraction that the two atoms have for the pair of electrons between them. In most covalent compounds it is easy to select the element that is oxidized, in general, this element is the one whose atoms have the weaker attraction for electrons. The carbon atom, for example, has four electrons in its outermost group, chlorine has seven, and oxygen has six. In a compound of carbon with oxygen or chlorine, there can be no doubt, therefore, as to which element attracts electrons more strongly. Chlorine and oxygen actually acquire electrons by pulling them off of some kinds of atoms, carbon seldom does this. Atoms of chlorine and oxygen require only one and two electrons, respectively, to complete stable groups of eight. Hence they would be expected to attract electrons that they share with carbon more strongly than does the latter. We might represent this condition — in a purely theoretical manner — by showing the pair of electrons that is shared as drawn closer to an atom of chlorine and farther from an atom of carbon,



instead of showing them exactly midway between the two atoms. Chlorine and carbon do not combine directly, but the compound CCl_4 can be made in other ways. Carbon and oxygen do combine, and theoretically the carbon atom shares two pairs of electrons with each atom of oxygen in carbon dioxide, CO_2 ,



When such reactions occur and compounds such as CCl_4 and CO_2 are produced, we think of the oxidized element as the one whose atoms contain the smaller number of electrons in their outermost groups. Sometimes, as in SO_2 , the atoms that combine contain the same number of electrons in this group, but even in the compounds formed by these atoms there is probably a difference in the attraction for electrons. The smaller atom — the one containing the smaller total

¹ We are thinking here of the numerical value of the valence number without regard to sign. A change from -3 to -1 or from -1 to 0 is regarded as a decrease in the negative valence number. A change from 0 to +1 or from +1 to +3 is regarded as an increase in positive valence number.

number of electrons and fewer electron groups around its nucleus — attracts electrons more strongly than the larger atom. This condition results because the shared electrons, or any electrons, can approach closer to the nucleus of the smaller atom, and therefore will be more firmly held by that atom than by the larger one. In such compounds we may think of the element composed of the larger atoms as the one that is oxidized. In sulfur dioxide, SO_2 , the sulfur atom is larger than the oxygen atom (see Table 3, page 54); and hence we consider sulfur as the element that is oxidized.

4. Reduction

In the reactions of oxygen with calcium and of chlorine with calcium and iron, atoms of the two non-metals acquire electrons from atoms of the metals, thereby becoming negatively charged ions. The negative valence numbers of chlorine and oxygen are increased in these reactions, that of chlorine changing from 0 to -1 , and that of oxygen from 0 to -2 . Similarly, in the reaction of carbon with oxygen, the negative valence number of oxygen is increased from 0 to -2 .

A reaction in which the negative valence number of some element is increased, or the positive valence number is decreased, is called *reduction*. Thus, if a transfer of electrons from one atom to another occurs, reduction involves a change in which atoms of some element gain electrons.

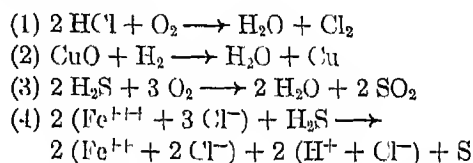
5. Oxidizing and Reducing Agents

In reactions involving oxidation and reduction, the substance that causes the oxidation of another substance is called the *oxidizing agent*, and the substance oxidized is called the *reducing agent*. In other words, atoms or ions of the oxidizing agent bring about an increase in the positive valence number or a decrease in the negative valence number of atoms or ions of the reducing agent; conversely, atoms or ions of the reducing agent bring about an increase in the negative valence number or a decrease in the positive valence number of atoms or ions of the oxidizing agent. Whenever transfers

of electrons occur, atoms or ions of the oxidizing agent acquire electrons, thereby increasing their negative charge or decreasing their positive charge. Atoms or ions of the reducing agent lose electrons, thereby increasing their positive charge or decreasing their negative charge.

Other Examples of Oxidation and Reduction

In order that we may further explain the use of the terms *oxidizing* and *reducing agents*, let us consider the following oxidation-reduction reactions:



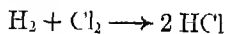
In reaction (1) the negative valence number of chlorine is decreased from -1 to 0, at the same time the negative valence number of oxygen is increased from 0 to -2 . Chlorine is oxidized and oxygen is reduced. Oxygen is the oxidizing agent, and hydrogen chloride — or, more strictly speaking, the chlorine of the hydrogen chloride — is the reducing agent. In reaction (2) copper is reduced and hydrogen is oxidized. In (3) sulfur is oxidized from -2 in H_2S to $+4$ in SO_2 . Oxygen is the oxidizing agent; and hydrogen sulfide — or, strictly speaking, the sulfur that it contains — is the reducing agent. In (4) iron is reduced from $+3$ to $+2$, and sulfur is oxidized from -2 to 0. The oxidizing agent in this reaction is the ferric ion, Fe^{+3} , of the ferric chloride, and the reducing agent is hydrogen sulfide.

Let us point out, finally, that each of the reactions that we have discussed above involves both oxidation and reduction. One substance is oxidized only when another is reduced.

6. Combustion

When oxygen reacts with other elements or with compounds, heat usually is liberated, but this is not always true. Nitrogen and

oxygen combine to form nitric oxide, for example, only when energy is absorbed. On the other hand, when carbon combines with oxygen to form carbon monoxide, CO, or carbon dioxide, CO₂, heat is liberated. The latter reaction may become so vigorous that light, as well as heat, is produced. Because of the heat that is liberated, the temperature rises, and finally the carbon becomes incandescent (emits light), as the temperature rises, more and more of the liberated energy appears in the form of light. The same reaction, occurring at lower temperatures, without the liberation of large quantities of heat and without the production of light, is spoken of as oxidation, or "slow" oxidation in contrast to the more rapid process that occurs during burning. *Combustion*, as the term is used in referring to reactions of oxygen with different substances, differs therefore from slower reactions of the same character only in the vigor of the reaction and in the forms and quantities in which energy is liberated. *As generally used, the term combustion refers to vigorous and rapid oxidation by oxygen attended by the liberation of energy in the form of heat and light.* Reactions other than those that involve oxygen, however, also liberate heat and light, and hence combustion is not strictly confined to the reactions of oxygen. A jet of acetylene, for example, burns brilliantly in chlorine: $C_2H_2 + Cl_2 \longrightarrow 2 HCl + 2 C$. The same is true of hydrogen



The capacity of causing combustion is not limited to the elements. Magnesium burns almost as brilliantly in carbon dioxide as it does in air. A glowing splint of wood placed in a sample of nitrous oxide (N₂O) bursts into flame, just as it does when it is placed in pure oxygen. Even water burns in an atmosphere of pure fluorine. The direct union with oxygen, therefore, is only one of many types of combustion, and combustion is merely rapid oxidation.

Although combustion is always accom-

panied by the evolution of light, the converse statement is not always true. Light may be produced by other means than combustion. Thus, the metal filament in an electric lamp does not burn in the ordinary sense. There is no oxygen in the lamp to support combustion. If there were, the filament would soon be oxidized completely, and the lamp would be worthless. Light is produced when the wire is heated to incandescence by the current of electricity that flows through it. The wire offers resistance to the current, and in overcoming this resistance some of the electrical energy is converted into heat and finally into light when the temperature reaches a point at which the tungsten filament becomes incandescent. In an electric lamp, the efficient use of electricity requires that as much of the energy as possible be converted into light instead of heat.

7 Kindling Temperature

Different substances must be heated to different temperatures before they ignite and continue to burn in air without further supply of heat from an outside source. Some substances, such as clay and sand, will not ignite at any temperature, because the elements that they contain have already combined with as much oxygen as they are capable of combining with, and further reaction is impossible. Some substances ignite at very low temperatures. White phosphorus, for example, ignites at about 35° C. Gasoline ignites at a lower temperature than kerosene, and kerosene at a lower temperature than motor oil. Ether ignites at a lower temperature than alcohol. Matches coated with paraffin, which ignites at a lower temperature than wood, are more easily ignited than matches not thus treated. The paraffin ignites soon after the head of the match is "struck", heat is liberated, the temperature rises, and finally the *kindling temperature* of the wood is reached.

The kindling temperature, at which a substance bursts into flames and combustion proceeds without further application of heat, is not a definite tem-

perature. It varies considerably depending upon the state of division of the substance. Iron and lead can be produced in small enough particles so that they will ignite without preliminary heating when they are poured from a container into the air. This effect is caused by the very large amount of surface exposed to the air. Finely divided particles offer much more surface than the same weight of the substance in one large mass.

The following experiment may be performed to demonstrate the effect of a fine state of division upon the kindling point and the rate of oxidation. Finely divided lead may be prepared by heating lead sulfate very slowly in a test tube. The compound decomposes, and all the elements except lead are expelled as gases. If the contents of the tube is not heated too rapidly or to a high temperature, lead may be prepared in a very fine state of division. After the reaction is complete, the tube should be tightly corked until the experiment is to be performed. When the cork is removed, and some of the lead is shaken into the air, combustion is spontaneous. The fine lead particles burn with flashes of light, evolving smoke that consists largely of particles of lead oxide (PbO).

The pressure of the air or oxygen in contact with the substance, and the presence (or absence) of catalysts, also have a pronounced effect upon the kindling temperature of a given substance.

8. Spontaneous Combustion

When a substance oxidizes slowly, just as much heat is liberated as when the same weight of the substance burns quickly. The temperature of substances that undergo slow oxidation does not become very high, because the heat is liberated slowly, and the surrounding objects, including the air, absorb it as rapidly as it is released. The energy liberated during the oxidation is scattered or dissipated. If slow oxidation occurs under conditions that do not permit heat to be dissipated as rapidly as it is liberated, the temperature slowly rises. With the rise in temperature, the oxidation rate also increases, and heat is liberated more rapidly. Eventually, the temperature of the kindling point of the substance is reached, and *spontaneous*

combustion results. Rags soaked in linseed and other oils often ignite spontaneously. The oils slowly oxidize, and because of the poor thermal conductivity of the rags, especially if they are thrown in a heap, the temperature of the mass increases. At higher temperatures the oil oxidizes more rapidly, raising the temperature of the rags to a still higher point, and so on, until the mass suddenly bursts into flame.

The slow oxidation of coal results in great losses. This is especially true of finely divided bituminous, or soft, coal. If the coal is properly stored in thin layers, the heat is lost rapidly. Under improper storage conditions, however, heat accumulates, and spontaneous combustion often results. The slow oxidation of coal, and fires resulting from spontaneous combustion, cause a very considerable loss each year. Fine coal should not be mixed with lump coal, since the former prevents the free circulation of air, a little circulation of air, of course, is worse than none at all, because it provides the oxygen that is necessary for oxidation, and thus liberates faster than it can remove the heat.

9. Flame

The combustion of many, but not all, substances is accompanied by the production of flames. Wood and coal, especially bituminous or soft coal, produce flames when they burn, but charcoal and coke do not. Flames are burning gases. When wood or soft coal is heated to the kindling point, or even before that temperature is reached, combustible gases or vapors are liberated. These substances usually ignite at a lower temperature than the residue of wood or coal, and their combustion produces the effect that we call flame. Charcoal is made from wood, and coke from coal, by heating wood or coal in the absence of air to prevent combustion. During the period of heating, volatile substances escape, and there is left a residue consisting, in each instance, principally of the element carbon. When charcoal and coke burn, therefore, no combustible vapors are

liberated, and there is no flame. The gas liberated when coke is made from coal is useful as a fuel; it is called *coal gas*.

When hydrogen burns, there is flame, since hydrogen is a gas, but the flame is almost without color. The flame produced by burning wood or coal, however, is colored yellow. Flames are usually colorless, if no solid particles are present in the burning gases, and if none are produced by the decomposition of substances in the gases as they burn. The hydrogen flame, for example, can be colored yellow if a small quantity of sodium chloride is volatilized (changed into vapor) and mixed with the burning hydrogen. Whenever sodium — either free sodium or a sodium compound — is heated until it is incandescent (begins to emit light), the color of the light that it produces is yellow. Incandescent barium chloride is green, potassium chloride, violet. When coal gas burns, some of the compounds in the gas decompose, and some free carbon is liberated. The fine particles of carbon emit colored light when they are sufficiently heated; the color depends upon the temperature. Similar effects are not produced when hydrogen burns, because there are no solid particles in the flame.

10 The Relation of Oxygen to Life

The energy of the steam engine comes indirectly from the burning of carbon, or compounds of carbon and hydrogen, in coal or gas to form, chiefly, carbon dioxide and water. The energy of the human body is derived from the oxidation of somewhat similar materials — foods and the waste materials of the body. Some food is oxidized directly, some is stored until it is needed, and some is used to build up tissues to take the place of those that have grown old and have been broken down in the different changes that occur in the body. The waste materials are oxidized to form soluble substances that can be carried away in the blood and eliminated, finally, through the kidneys and lungs. A part of the energy released during oxidation is used to maintain the proper temperature of the body.

In the lungs, oxygen passes into the blood, where it combines with hemoglobin to form

red *oxy-hemoglobin*, which is responsible for the color of blood in the arteries. In this form it is carried to the tissues of different parts of the body, where it is released from its combination with hemoglobin and is consumed in the oxidation of food and waste materials. The blood, now containing hemoglobin, returns through the veins to the lungs, there it liberates carbon dioxide and collects another supply of oxygen.

CONDITIONS THAT INFLUENCE THE RATE OF OXIDATION AND OTHER REACTIONS

11 The Conditions

Warm milk becomes sour more quickly than milk placed in the refrigerator. Substances burn in pure oxygen more vigorously than in air. In the presence of finely divided platinum, hydrogen and oxygen combine to form water much more rapidly than they do, at the same temperature, when platinum is absent. Powdered coal oxidizes more rapidly than lump coal. These statements call attention to four conditions that affect the speed of oxidation and other types of reactions: temperature, concentration, catalysts, and the state of division or amount of surface exposed. Warm milk becomes sour more rapidly than cold milk, because the chemical change involved occurs much more rapidly at the higher temperature; oxidation is more rapid in pure oxygen than in air, because the former is more concentrated than the latter; platinum catalyzes the reaction of hydrogen and oxygen, and coal in powdered form oxidizes more rapidly than in lump form, because more surface is exposed to the action of the oxygen in the air by the fine particles than by the lumps.

12 Temperature

In general, the speed of a reaction is doubled for a rise of 10° in the temperature of the substances involved in the reaction. If the same rule holds for very low temperatures, a reaction completed in two minutes

at 20° would require about seven and one half years for completion at -180°, a temperature that can be reached by means of liquid air. One effect of the change in temperature can be readily understood. The velocities of the molecules are increased as the temperature rises, and hence the reacting molecules meet more frequently, and more molecules have the opportunity of participating in the reaction in a given period of time than would at a lower temperature. An increase in temperature, therefore, results in the production of larger quantities of the products of the reaction in the same period of time.

The explanation offered above does not explain, however, all variations in the speeds of reactions at different temperatures. Sometimes a change of 10° increases the speed of a reaction many times. The cause of such effects will be discussed in Chapter 23.

13 Concentration

Pure oxygen supports combustion more readily and more rapidly than air, because four fifths of the air is nitrogen, which takes no part in the reaction. Pure oxygen is more concentrated, i.e., it contains more oxygen per liter than air. And pure oxygen under pressure is still more concentrated than pure oxygen under atmospheric pressure. Concentration is a measure of the number of molecules of a reacting substance in a unit of volume, such as the cubic centimeter or the liter. We should not confuse concentration with the total quantity of a substance that may be present. There is about the same quantity of oxygen, for example, in five liters of air as in one liter of pure oxygen. In the former, however, the concentration is only one fifth as great as in the latter. The effect of increased concentration upon the speed of a reaction is not difficult to understand. Naturally, the more molecules of a reacting substance in a given volume, the greater will be the number of chances that these molecules will react with the molecules of another substance in the same space.

14 Catalysts

The effect of platinum upon the reaction of hydrogen and oxygen, and the similar effect of other substances on other reactions, is called *catalysis*, and the agent producing the effect is a *catalyst*. A catalyst does not start a reaction, it merely changes the reaction's velocity. Many reactions occur so slowly at low temperatures that no change is perceptible. But the proper catalyst may increase the velocity of such a reaction, without changing the temperature or other conditions, and thus the effects of a reaction that otherwise does not appear to occur, because it is so slow, become very noticeable.

Some catalysts are useful because they retard certain reactions, but most of the catalysts used commercially are valuable because they accelerate reactions that otherwise would be too slow to be practicable. This use of a catalyst is frequently of considerable importance in the manufacturing industries, for it allows a greater quantity of the products of a reaction to be manufactured in a definite period of time. The use of a catalyst is especially practical when undesirable results stem from raising the temperature to speed the reaction. Although an increase in temperature always results in an increase in speed, it often happens that a reaction is less complete at the higher temperature than it would be if it were carried out at a lower temperature. At high temperatures, therefore, the product may be made more rapidly, but the total amount that can be produced is smaller than the amount that can be formed from the same quantities of starting materials at a lower temperature. Furthermore, some substances are decomposed, forming products that are not wanted, when the temperature is raised. When such reactions occur, a catalyst is desirable in order that the speed may be increased at low temperature without decreasing the total possible yield.

15 State of Division

When substances — liquids and solids — are finely divided into small grains, threads, or drops, the amount of surface is greatly increased. This increase in surface permits better contact and hence more chances of

reaction than are possible when the same substances are used in coarser states of division. An extension of the surface really amounts to an increase in the concentration of the reacting material. Many examples can be cited to show this effect. Shavings, splinters, or kindling burn much more rapidly than the same quantity of wood in the form of a log. Lumps of coal burn slowly, but a mixture of coal dust and air can be exploded with a spark or small flame — and this very reaction accounts for many mine explosions. Similar explosions sometimes occur in flour mills, or wherever finely divided combustible materials of any kind are mixed with air.

16 The Effect of Chemical Characteristics of Reacting Substances

In addition to the conditions already described, the chemical natures of substances — the kinds of atoms that they contain and the manner in which these atoms are held together — play an important part in determining the speed with which they react with one another. For example, at a given temperature and for a constant concentration of oxygen, some metals combine much more rapidly with oxygen than others. Similar differences are noticeable in the reactions of the halogens — fluorine, chlorine, bromine, and iodine — with hydrogen. Fluorine reacts with hydrogen explosively even at -250° , a mixture of hydrogen and chlorine can be exploded by exposure to a bright light; bromine and hydrogen react readily when heated, and the reaction between iodine and hydrogen is not complete under any conditions. Differences in the rates of the reactions of different elements, under the same conditions, can be explained only by considering differences in their chemical energy and in the structures of their atoms and molecules.

OZONE

17. An Allotropic Modification of Oxygen

Shortly after the discovery of oxygen, experiments in which electric sparks were

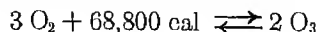
passed through the gas at ordinary temperatures resulted in the production of a substance possessing a peculiar odor. Later the odor was found to belong to a substance produced from oxygen under the influence of the electric sparks. Investigation of this substance showed that it resembled oxygen in many respects, but was not as stable and possessed much greater chemical activity. A study of its composition revealed that its molecules contained only atoms of oxygen. It is now known as *ozone* and is classified as an *allotropic modification* of oxygen. *Different forms of the same physical state of a substance are called allotropic modifications of the substance.* Several of the elements and some compounds exist in different forms analogous to ozone and ordinary oxygen.

Strictly speaking, oxygen and ozone are different substances, although both are composed of a single kind of atom. We may consider them as different substances because (1) their molecules have different composition, (2) they have different properties, and (3) they contain, for the same unit of weight, different quantities of chemical energy.

The molecule of ozone is represented by the formula O_3 , while the molecule of ordinary oxygen is O_2 . The change from the latter to the former therefore involves the addition of an atom of oxygen to each molecule. The behavior of ozone indicates that the added atom is rather loosely held.

18 Preparation

The equation for the reaction by which ozone is produced from oxygen is



The reaction requires the absorption of considerable energy, but this cannot be supplied in the form of heat, since ozone is not stable at elevated temperatures. The substance is usually prepared by passing oxygen or air between two metal plates, which are highly charged electrically. This results in the occurrence of a silent electric discharge in the

oxygen or air between the plates. A common form of ozonizing apparatus is shown in Figure 53. The inner surface of the inner tube and the outer surface of the outer tube are covered with tin foil. These two layers of tin foil act as the metallic plates between which the discharge occurs. They are connected to an induction coil. The electric discharge can be observed in a dark room as a pale blue glow within the apparatus. The silent electric discharge is well adapted to the production of ozone, since it does not have a heating effect. Only a small percentage of the oxygen passed through the apparatus is changed, ordinarily, into ozone.

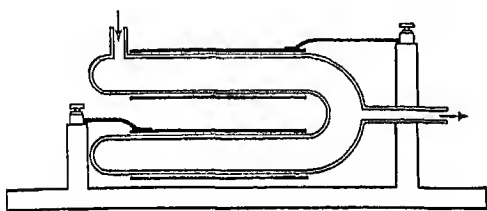


Figure 53 Apparatus Used to Produce Ozone by Means of an Electrical Discharge

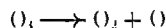
From cold, dry oxygen, yields of 6 to 10 per cent may be obtained. Some of the commercial forms of ozonizing equipment will convert from 16 to 18 per cent of the oxygen into ozone. Moisture and high temperature reduce the yield, but if the temperature is lowered by use of liquid air, yields as high as 90 per cent can be attained. At the temperature attained in this manner, the ozone separates as a liquid, since it is more readily liquefied than ordinary oxygen.

Ozone is also produced in small amounts in other ways. Some is produced by lightning flashes, and by the action of ultraviolet light upon the oxygen in the upper portions of the atmosphere. The slow oxidation of a piece of yellow phosphorus that is partially exposed to the air and partially covered with water results in the formation of traces of ozone. Some is also liberated in the electrolysis of water and in other reactions in which oxidizing conditions are especially favorable.

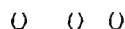
19. Properties

Ozone is heavier than oxygen, one liter at 0°C weighs 2.144 g. The gas has a pale blue color, and the liquid, which boils at -112.3°C , is deep blue. It is much more soluble in water than ordinary oxygen, at 0°C , 50 liters of ozone dissolve in 1 liter of water, although the pressure of the gas has a considerable effect upon the quantity that dissolves. The solubility quoted is for the average atmospheric pressure at sea level.

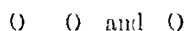
The chemical properties of ozone are similar to those of oxygen, except for its greater chemical activity. Some of the metals, such as silver and mercury, which are not affected by oxygen, are tarnished rapidly by the formation of their oxides when they are exposed to ozone. When ozone decomposes, it liberates oxygen in the atomic form.



In the molecule of ozone the atoms of oxygen share electrons, probably in the manner shown in the following theoretical formula:



When it decomposes, this molecule forms



The single atoms of oxygen can acquire two more electrons each by sharing electrons with others of their own kind or by reacting with other kinds of atoms. They are, therefore, much more active than molecules of O_2 . When the latter react, the molecules must first be broken up into atoms, since these are the particles that actually participate in chemical changes. Energy must be absorbed to bring about such a change, while the atoms liberated by ozone are ready to react in the condition in which they already exist.

The production of ozone from ordinary oxygen requires that a large quantity of energy be absorbed. This energy, which amounts to about 700 calories per gram, is supplied by the electric discharge, or by the chemical energy of reacting substances as,

for example, in the production of ozone by the slow oxidation of phosphorus. When ozone decomposes, an amount of energy equivalent to that which was absorbed in its formation is liberated as heat. Ozone therefore contains more chemical energy than ordinary oxygen. This greater energy content is largely responsible for the differences between the two forms of oxygen and especially for the difference in chemical activity. The rate at which ozone decomposes is greatly increased by elevated temperatures and the presence of moisture.

Ozone is usually detected by its characteristic odor. It is also detected by means of a strip of filter paper that has been moistened with a solution of potassium iodide and starch. Ozone reacts with potassium iodide to liberate iodine (displacement of iodine by oxygen). The free iodine then gives a blue color with the starch.

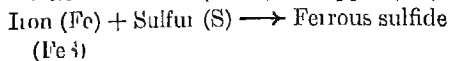
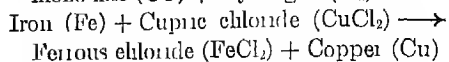
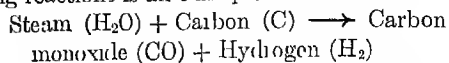
20 Uses

Ozone, or air containing varying amounts of ozone, has a number of uses, which are based upon the active oxidizing properties of the substance. When ozone reacts with certain colored materials, it oxidizes them, forming colorless products. This reaction is called *bleaching*. Cloth, flour, starch, and other materials are sometimes bleached in this manner. Ozone is also used as a disinfectant and deodorant. In Europe it is used to sterilize drinking water. But because of the difficulty of producing it, the cost is high and its uses are limited.

Review Exercises

- 1 Define oxidation, combustion, kindling point, spontaneous combustion.
- 2 Paper is composed largely of cellulose, $C_6H_{10}O_5$, in which the carbon and hydrogen are already combined with oxygen. How can paper burn, if burning means that these elements combine with more oxygen?
- 3 Why can this reaction (question 2) properly be called a case of oxidation?
- 4 Using the term oxidation as it is defined in

this chapter, explain why each of the following reactions is an example of oxidation.



- 5 Name the oxidizing agent in each of the reactions of question 4.
- 6 How do fires sometimes originate spontaneously in barns filled with hay? Why will hay that is very wet not ignite in this way?
- 7 Explain the meaning of the term concentration and show how the concentration of oxygen affects the rate of combustion.
- 8 Why does powdered coal when mixed with air burn more rapidly than large lumps of coal?
- 9 For what purpose and in what manner is oxygen used in the body? Where do the chemical changes involving oxygen occur?
- 10 How is oxygen transported from the lungs to the different parts of the body?
- 11 Discuss the accuracy of the following statement: Oxidation is a reaction in which oxygen combines with a substance.
- 12 When calcium, Ca, reacts with chlorine, calcium chloride is produced, calcium is oxidized by chlorine. How does this statement agree with the general definition of oxidation?
- 13 Oxidizing agents are added as ingredients in fireworks and matches. What purpose do they serve?
- 14 Why does coke burn without a flame? What is a flame?
- 15 Refer to Figures 26 and 34. Which element should be designated as the one that is oxidized when sulfur and oxygen react to form sulfur dioxide, SO_2 ?
- 16 How can the spontaneous combustion of powdered coal or oily waste be prevented?
- 17 When wood burns, energy is released as heat. What was the original source of this energy?
- 18 Why does fanning a fire cause combustion to proceed more vigorously?
- 19 How does water aid in extinguishing a fire? (Recall the definition of kindling point.)
- 20 Why does closing the damper below a fire in

- a stove reduce the rate of combustion of fuel?
21. When gas is ignited at the end of a tube, why does the gas in the tube not burn?
 22. Why is an electric lamp a safer source of light in a dusty coal mine than a candle flame?
 23. What increase in surface would result from splitting a block of wood measuring 3 in. by 3 in. by 3 in. into two blocks each measuring 3 in. by 3 in. by $1\frac{1}{2}$ in.?
 24. Which of the following statements about catalysts are true?
 - (a) A catalyst starts a reaction that otherwise does not occur
 - (b) The chemical energy content of a catalyst is changed when it is used (as a catalyst) in a reaction
 - (c) A catalyst is not converted into a different substance when it is used in a reaction
 - (d) The use of a catalyst is the only method by which the speed of a reaction can be changed
 - (e) A catalyst always increases the speed of a reaction if it has any effect at all
 - (f) In some reactions, a catalyst is used to reduce the speed
 25. Why is finely divided carbon or coal mixed with liquid oxygen or air when the latter is used as an explosive?
 26. What is the advantage of storing coal under water?

References for Further Reading

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THE GAS LAWS AND THE KINETIC MOLECULAR THEORY

... If men were willing to regard the advancement of philosophy, more than their own reputations, it were easy to make them sensible, that one of the most considerable services they could do to the world is to set themselves diligently to make experiments and collect observations without attempting to establish theories upon them before they have taken notice of all the phenomena that are to be solved

ROBERT BOYLE

1 Introduction

We are now to study the general physical properties and behavior of matter in its gaseous state. Although these properties are very different for the three states of matter — solid, liquid, and gaseous — this study of gases should add something to our information about the other states, and to our understanding of them, because fundamentally all the states of a substance are composed of the same kind of matter, and the three states are only its three physical forms. Information concerning one of these forms should, therefore, assist us in formulating at least reasonable theories concerning the others.

The study of gases is especially important at this point in our story for the following reasons:

- (1) It provides further evidence in support of the atomic theory and makes clear the necessity for distinguishing between atoms and molecules of some elements. It also gives some indication of the number of atoms in a molecule of oxygen, hydrogen, and certain other gaseous elements.
- (2) It provides us with a method by which the weights of molecules of different substances can be compared — a method of determining molecular weights.
- (3) It gave to chemistry the first means of determining the relative numbers of different kinds of atoms that combine to form compounds, and hence it provided one basis for determining the composition of a molecule, or the formula of a compound.
- (4) The laws that deal with the behavior of gases must be understood before one can work accurately with gases in laboratory experiments or on a larger scale. The weights of equal volumes of two gases, for example, cannot be compared, until one understands the conditions under which the two volumes can be regarded as equal, unless the conditions of temperature and pressure are exactly the same, a liter of oxygen collected today will not represent the same quantity of oxygen as a liter collected tomorrow.

2. Differences Among Gases, Liquids, and Solids

A single solid portion of matter retains its form and occupies the same space, regardless of the container in which it is placed. A liquid fills its container to a certain level, the height of which above the bottom of the vessel is determined by the quantity of liquid and the shape and size of the vessel. A liquid differs from a solid in its ability to flow and

to fill its container uniformly in all directions except vertically. A solid in a fine, granular state, such as sugar, salt, or sand, can be poured and tends to flatten out when placed in a heap. This condition of a solid approaches somewhat the condition of a liquid. The difference lies in the size of the particles of the liquid as compared with the size of the grains of the solid. Gases are still less restricted in movement than liquids, in fact, in an open vessel gases appear to be restricted scarcely at all. They expand rapidly and in a short time are uniformly distributed throughout the entire volume of a closed container. If the container is not closed, they continue to expand indefinitely, even into space that is already occupied by other gases. This tendency of a gas to expand indefinitely is called *diffusion*. The rate of diffusion is the rate at which the gas passes through a very small opening or through a porous wall.

As a matter of fact, liquids and even solids may fill the entire space, in a certain sense, when they are placed in a closed vessel. Water placed in the lower part of a closed vessel evaporates, and *water vapor* fills the container above the surface of the liquid. There is water, therefore, in all parts of the enclosed space, but the water is not uniformly distributed in the container. Most of it is below the surface of the liquid. In a similar manner, we may think of many solids and liquids as filling their containers, but as in the case of water, the quantity of the substance in that portion of the vessel which is not occupied by the liquid or the solid is very small, so small in many cases that one cannot easily detect it. The difference in this respect between gases on the one hand and liquids and solids on the other lies in the fact that gases are *homogeneously* distributed throughout the volumes of their containers.

Gases also differ from solids and liquids in the relative ease with which they can be compressed. We are familiar, for example, with the relative ease with which a rather large volume of air, measured under the ordinary conditions of the atmosphere, can be forced into an automobile tire. Solids and liquids are not easily compressed. The

volume of a gas is decreased by one half when the pressure upon it is only doubled; to produce the same effect upon the volume of a liquid or a solid, the pressure would have to be increased many thousand fold.

When gases are heated, they exhibit a strong tendency to expand, and do so unless they are confined. If the gas is heated in a closed container, the pressure upon the walls is increased, and the volume remains unchanged, because the walls of the container prevent expansion. Upon cooling, the pressure is decreased, but the volume still remains the same, since the gas fills its container as long as it remains a gas.

Finally, the densities of gases (density equals mass divided by volume) are small in comparison with the densities of liquids and solids. One gram of liquid water occupies 1 ml at 4°C, and at other temperatures the volume is only slightly different. When this same weight of water is changed into water vapor, its volume is increased about 1500 times. The density of (liquid) water, therefore, is about 1500 times as great as the density of water vapor. We must note, however, that the densities of both the liquid and the vapor vary under different conditions of temperature and also, for gases especially, under different conditions of pressure. As the temperature increases, a gas expands, and the weight per unit of volume (1 ml or 1 liter) decreases. Under increased pressure, the same weight of a gas is compressed until it occupies less space, therefore, one unit of volume contains more of the gas and weighs more than it does at a lower pressure. The density of a gas is almost always expressed as the weight of *one liter* at some definite temperature (usually 0°C) and pressure (usually the average pressure of the atmosphere at sea level).

Gases are characterized, then, by pronounced capacity to expand and to diffuse, by relatively slight resistance to forces that tend to compress them, and by relatively small densities. We do not mean to leave the impression that only gases expand, diffuse,

and can be compressed. Some liquids, and to a much smaller extent some solids, if placed in contact, tend to diffuse one into the other. Solids and liquids also show changes in volume under different conditions of temperature and pressure. These effects, however, are much smaller than for gases.

3. The Pressure Exerted by a Gas

The manner in which gases *exert* pressure is an important difference between them and liquids or solids. As an example of the pressure exerted by a gas, let us consider the pressure of the atmosphere. When air is forced into a closed vessel, the pressure upon the walls is increased, indeed, the walls of the vessel may burst, and the effect may be similar to that of an explosion, if a large quantity of air is very rapidly forced into the vessel. A vessel containing air in contact with the atmosphere is also subjected to pressure. An "empty" tin can retains its form, because it contains air, which exerts a pressure equal to that from without, the can is in fact not empty. If it is closed and connected to a pump that removes the air within it, and if the walls are not strong enough to resist the pressure of the atmosphere from without, the can crumples as the air is removed.

The pressure of the atmosphere is sometimes said to be caused by its weight, but if

this were true, the pressure of the gas would be exerted only in a downward direction — toward the center of the earth. It is true that the pressure of a bar of lead upon a table does depend upon the weight of the bar and is exerted in a downward direction, the bar does not exert pressure in an upward direction or to any side. But within a box containing air or any other gas, there is just as much pressure, for the same surface, upon the top of the box as upon the bottom. If we force more air into the box, the increase in pressure is distributed equally over all the walls. We must seek, therefore, an explanation of the pressure of gases that does not depend upon weight. And before we can determine the most likely explanation, we must learn more about the behavior of gases in general.

4. The Barometer

The pressure of the atmosphere is measured by a barometer (Figure 54). A simple form of barometer can be prepared by filling a tube, closed at one end and about 80–85 cms in length, with dry mercury. The tube is inverted so that the open end lies beneath the surface of mercury in an open vessel. Care must be taken during the inversion of the tube to see that no air enters it. When the open end is placed beneath the surface of mercury in the vessel, the height of the mercury column falls, leaving a vacuum at the top. There is, then, no pressure, or only a negligible pressure due to a little mercury vapor, above the surface of the mercury in the closed tube. Since mercury is a liquid, it would continue to fall until the level was the same in the vessel and in the tube, if there were no pressure upon the surface of the mercury in the open vessel to hold the column above this level. Such pressure is exerted by the atmosphere — a pressure that varies from place to place on the earth's surface, and from day to day, and even from hour to hour, at any one place. The average pressure at sea level will support a column of mercury 760 mm in



Figure 54 Two Forms of the Barometer

height. The height of the mercury column is the distance between the two mercury levels, one in the open vessel and the other inside the barometer tube. Another form of barometer tube consists of two arms, one closed and one open to the atmosphere (Figure 54). In this type of instrument the atmospheric pressure is equal to that of a column of mercury whose height is the distance between the mercury levels in the two arms of the tube.

The pressures exerted by all gases can be measured in a manner similar to that employed in determining the pressure of the atmosphere. We are accustomed, therefore, to speak of the pressure exerted by a gas in terms of the height of the column of mercury that the pressure will support against the action of gravity -- the earth's attraction. The pressure measured by a column 760 mm in height is called *one atmosphere*. When we state that the pressure of a gas is 200 atmospheres, for example, we mean that the pressure is approximately 200 times the average pressure exerted by the atmosphere at sea level.

5. Boyle's Law The Relation of Pressure to Volume

We can easily demonstrate (as in Figure 55) the relation between the pressure exerted by a gas and the volume that the gas occupies. We understand, of course, that the temperature must remain constant during the comparison of the volumes occupied by a

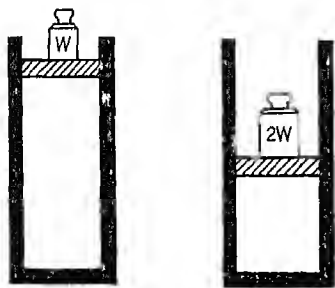


Figure 55. Boyle's Law

The relation between the volume of a gas and the pressure exerted upon it

definite quantity of a gas under different pressures, because changes in temperature also affect the volume, or if the volume cannot change because of the walls of the containing vessel, the pressure changes as the temperature is varied. The quantity (weight) of the gas must also remain constant.

If the pressure exerted upon some definite quantity of gas is doubled, the pressure exerted by the gas is also doubled. The greater the pressure applied to the gas, the more pressure it exerts upon the walls of its container. Consideration of Figure 55 shows that this is true. If the pressures from above and from below were not equal, the weight that produces the pressure upon the gas would not be supported. The fact that this weight assumes a fixed position indicates that the pressure from below is equal to the pressure from above.

An increase in the pressure exerted upon a gas (and by a gas), as indicated by the use of a larger weight in Figure 55, is accompanied by a decrease in volume, provided the construction of the vessel makes this possible. We find, for example, that the volume is decreased to one half of the original volume, when the pressure is doubled. On the other hand, a sample of gas that exerts a pressure of one atmosphere, when its volume is one liter, exerts a pressure of one half of an atmosphere, when it is allowed to expand into a larger vessel in which the volume is two liters, provided the temperature does not change.

At constant temperature, the volume of a definite weight of a gas and its pressure are inversely proportional. This law was first recognized and stated by Robert Boyle in 1660. It is now called Boyle's Law. The law can also be stated in the form of the following equation.

$$p_1 v_1 = p_2 v_2,$$

in which p_1 and p_2 represent two pressures and v_1 and v_2 represent the corresponding volumes. This equation is nothing more or less than a brief and concise statement to the

effect that the product of the pressure and the volume of a gas (at constant temperature) is a constant. If either one changes, then the other must change in the opposite direction and to the same extent.

In order that we may explain the expression "inversely proportional," let us change the equation as it is stated above by dividing both sides by p_1v_1 . We thus obtain

$$\frac{p_1}{p_2} = \frac{v_2}{v_1}$$

It will be noted in the two ratios, or fractions, that the two subscripts are in a different (inverse) order, hence the pressure and the volume are seen to be inversely proportional.

6. An Experiment to Demonstrate Boyle's Law

Boyle's law can be verified by means of the simple apparatus shown in Figure 56. The pressure upon the gas confined in the space *C* is equal to the pressure of the atmosphere plus the pressure exerted by a column of mercury equal to the difference between the levels in *A* and *B*. Let us assume that the atmospheric pressure is 750 mm, and the volume is 10 ml. In Figure 56, the pressure has been increased by raising the height of the mercury level in *B* so that the difference between the two levels is 10 mm. The total pressure upon the gas in *C* is now 760 mm, and the volume of the gas in *C* is now found to be 9.87 ml. The ratio of this volume to the volume originally occupied by the gas is the same as the ratio of the first pressure to the second:

$$9.87/10 = 750/760$$

or

$$10 \times 750 = 760 \times 9.87,$$

which can also be written in the form of the general equation,

$$p_1v_1 = p_2v_2,$$

in which p_1 and v_1 are the pressure and volume, respectively, under the first set of conditions, and p_2 and v_2 are the pressure and volume under the second set of conditions. Any slight difference observed between the two ratios is due to in-

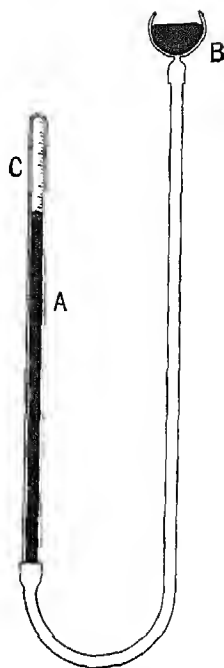


Figure 56 Apparatus Used in Verifying Boyle's Law

accuracies in reading the volumes or measuring the pressure, to slight changes in temperature, or to slight deviations in the behavior of gases from that predicted by Boyle's law (page 89).

The experiment described above deals with data that resemble those of an actual series of measurements in the laboratory. Somewhat simpler data—simpler to analyze and understand—may aid the student in studying this law, although it is not likely that an actual experiment would result in data that could be expressed by whole numbers. If 64 liters of a gas at 1 atmosphere is subjected, at constant temperature, to increasing pressure, the relation between pressure and volume at different pressures will be found to be as follows:

Pressure	Volume	Product, p_v
1 atmosphere	64 liters	64
2 "	32 "	64
4 "	16 "	64
8 "	8 "	64
16 "	4 "	64
32 "	2 "	64
64 "	1 "	64

7 Calculations Based upon Boyle's Law

It is often necessary to calculate the volume of

a definite quantity of a gas at some pressure that is different from the pressure under which the volume is actually measured. This may be done by applying the equation for Boyle's law as given above. To compare the weights of equal volumes of different gases, for example, it is necessary that their volumes should be determined at the same pressure. If we should measure two liters of even the same gas, one at one pressure and the other at another pressure, the two liters would not contain the same weight of the gas. It is inconvenient, and often impossible, to measure the volumes of all gases under the same pressure, but this is not necessary if we select some standard pressure. We can then measure the volumes of different gases at any convenient pressures and calculate the volumes which the same quantities of the gases would occupy at the standard pressure. The standard that has been selected is 760 mm. of mercury. If we measure one liter each of two gases at different pressures, the volume of each at the standard pressure, of course, will not be one liter, but this is not essential. If it turns out that we have, at standard pressure, 0.6 liter of one gas weighing 2 g. and 0.7 liter of the other weighing 3 g., the weight of a liter of each can be calculated very easily

$$\begin{aligned} 2 \times 1/0.6 &= 3.33 \text{ g.} = \text{the weight of 1 liter of A} \\ 3 \times 1/0.7 &= 4.286 \text{ g.} = \text{the weight of 1 liter of B.} \end{aligned}$$

As an illustration, let us say that it is necessary that we measure the volume of a gas at a pressure of 720 mm., although we wish to determine the volume of the same quantity of the gas at 760 mm. of pressure. We find the volume at the observed pressure to be, let us say, 100 ml. It is evident that the volume at 760 mm. will be less than 100 ml., since the pressure is increased. In making the necessary calculation we multiply the observed volume by a fraction, in which we write the smaller pressure as the numerator and the larger pressure as the denominator

$$100 \times 720/760 = 100 \times 0.947 = 94.7 \text{ ml.}$$

The lower pressure is 0.947 of the higher pressure and, in accordance with Boyle's law, the volume at the higher pressure is 0.947, or 94.7 per cent, of the volume at the lower pressure.

If the second pressure is lower than that at which the volume is measured, the calculation is made in the same manner, except that the fraction by which the observed volume is multiplied

must contain the larger pressure in the numerator. If 100 ml. of the gas is measured at 760 mm., the volume at 720 mm. is found as follows

$$100 \times 760/720 = 100 \times 1.055 = 105.5 \text{ ml.}$$

In accordance with the method of calculation which we have just illustrated, we may write the following general equation

$$v_2 = v_1 \times p_1/p_2,$$

where v_1 is the volume of gas as observed at the pressure p_1 , and v_2 is the volume at p_2 . This equation is nothing more than a modified form of the equation stated previously

$$\begin{aligned} p_2 v_2 &= p_1 v_1 \\ v_2 &= \frac{p_1 v_1}{p_2}. \end{aligned}$$

The two equations are thus shown to be different forms of the same statement.

8 Volume and Temperature

It is a well-known fact that a gas tends to expand as its temperature rises. If the expansion is prevented by the walls of the vessel that contains the gas, there will be no change in volume, and the increased temperature will produce an increase in the pressure of the gas. But if the gas is allowed to expand, with increasing temperature against a constant pressure, one observes a very definite relation between the rise in temperature and the increase in volume or between the fall in temperature and the decrease in volume. A temperature change of one degree causes a change in the volume occupied by the gas equal to $1/273$ of the volume which the gas occupies at 0°C ., provided that there is no change in pressure.

9 Absolute Temperature Scale

Let us assume that a certain weight of a gas occupies 273 ml. when the volume is measured at 0°C . Since the volume decreases $1/273$ of the volume at 0° for each drop of one degree, the volume at -273°C should be zero. The temperature -273°C . is called, therefore, the *Absolute zero*. The scale of Absolute temperature is based upon

this zero. It will be remembered that this change of volume applies only to gases, and that all gases can be liquefied at temperatures above -273°C . Hence, the question of just what volume a gas does occupy at -273° is avoided, gases do not exist at this temperature. *Absolute zero is the temperature at which a gas, if it did exist, theoretically would possess zero volume.* It might be better to state that at temperatures at which a substance does exist as a gas, the volume of the gas changes with the temperature in a manner that indicates the volume would be zero at -273°C .

The relation between the Centigrade and Absolute temperature scales is shown below

	Centigrade	Absolute
Water boils	100°	373°
Water freezes	0°	273°
Absolute zero	-273°	0°

10 Charles's Law

Let us compare the volumes that a certain sample of gas occupies at 0°C , 100°C , and -100°C . Let us select a sample that occupies 273 ml at 0° ; this volume is a convenient one to use in explaining the manner in which the volume varies as the temperature changes. The pressure is constant. The volume at 100° and at -100° can now be calculated by applying the rule which states that the volume increases (or decreases, depending upon the direction of the change in temperature) $1/273$ of the volume at 0° for each change of 1° Centigrade.

Volume at $-100^{\circ} =$

$$273 \text{ ml} - \left(\frac{100}{273} \times 273 \text{ ml} \right) = 173 \text{ ml}$$

Volume at $100^{\circ} =$

$$273 \text{ ml} + \left(\frac{100}{273} \times 273 \text{ ml} \right) = 373 \text{ ml}$$

Centigrade Temperature	Absolute Temperature	Volume
0°	273°	273 ml
100°	373°	373 ml
-100°	173°	173 ml

We note that there is no direct or inverse relation between the changes in Centigrade temperature and the changes in volume, the ratio of any two Centigrade temperatures is entirely different from the ratio of the volumes of the gas at these temperatures, and one ratio is not the inverse form of the other. But the Absolute temperatures and the volumes are directly proportional; that is, when the Absolute temperature is increased from 273° to 373° , the volume is increased in the same proportion, from 273 to 373 ml. This statement expresses Charles's Law. *If the pressure does not change, the volume of a definite quantity of gas varies directly with the Absolute temperature.* Gay-Lussac stated the same principle almost at the same time as Charles (1801), and this is sometimes called the Law of Gay-Lussac.

We can express this law in the following mathematical form, using v_1 and v_2 for the two volumes and T_1 and T_2 for the two corresponding Absolute temperatures:

$$\frac{v_1}{v_2} = \frac{T_1}{T_2}$$

If, for example, the volume is 373 ml at 100°C or 373°Abs , the volume at -100°C or 173°Abs . can be calculated as follows

$$\frac{373 \text{ ml}}{v_{173^{\circ}}} = \frac{373^{\circ}}{173^{\circ}}.$$

From this equation it follows that

$$v_{173^{\circ}} \times 373^{\circ} = 373 \text{ ml} \times 173^{\circ} \quad \text{and} \\ v_{173^{\circ}} = 373 \text{ ml} \times \frac{173^{\circ}}{373^{\circ}} = 173 \text{ ml}$$

This shows how the volume of a definite quantity of a gas at -100° can be calculated from the volume at 100° and the two Absolute temperatures. The Charles's law equation for the general case in which the volume at one temperature, T_1 , is v_1 , and the volume at the second temperature, T_2 , is v_2 may be stated as follows.

$$v_2 = v_1 \times T_2/T_1$$

11. Calculation of Gaseous Volumes and Pressures by Charles's Law

The equation of Charles's law can be used to calculate the volume of any gas at any given temperature from the known volume at another temperature, pressure remaining constant. It is not necessary, however, to remember even this simple equation in making these calculations. For example, suppose a calculation is needed for the volume at 10°C of a gas which occupies 100 ml. at 45°C . The two Absolute temperatures are 283° and 318° , respectively, and the volumes are v_2 and 100 ml. To find the new volume, v_2 , the old volume, v_1 , must be multiplied by a fraction. In this case the smaller of the two Absolute temperatures must be made the numerator of this fraction, since it is evident that the new volume will be smaller than the old because of the tendency of a gas to contract as the temperature is lowered. Accordingly,

$$v_2 = 100 \times 283/318 = 89 \text{ ml.},$$

which can be written in the form of the general equation already given

$$v_2 = v_1 \times T_2/T_1$$

It is generally more satisfactory to solve a problem, first, from a consideration of the facts involved, arriving at the solution by a line of reasoning similar to that which we have followed in this case. The general mathematical equation which applies to the problem and all others like it can then be derived from the solution first obtained. If we can do this, there can be little doubt of our understanding the principles upon which the solution of the problem is based. If we depend upon the substitution of the correct values for the symbols in the general equation, we may, or we may not, understand these principles.

So far, we have considered cases in which the pressure is constant and the volume varies with the Absolute temperature. Let us now consider the change in the pressure of a definite weight of a gas with changes in temperature, when the volume remains constant. Under these conditions, it is found that the pressure is also directly proportional to the Absolute temperature, and we may write

$$p_2 = p_1 \times T_2/T_1,$$

where p_1 is the pressure exerted by the gas at the Absolute temperature T_1 , and p_2 is the pressure when the Absolute temperature is T_2 .

12. Standard Conditions of Temperature and Pressure

In the comparison of the weights of equal volumes of different gases a *standard pressure* (as we have already stated on page 91) and a *standard temperature* must be selected. If, for example, we wish to compare the weight of one liter each of two gases, it is necessary that the two volumes should be measured at the same pressure and at the same temperature. A liter of a gas measured at one temperature does not weigh the same as a liter measured at some other temperature, under constant pressure, and the same is true of liters of the same gas measured under constant temperature conditions but under different pressures. The standard condition of temperature is 0°C , or 273° Absolute, and the standard pressure, as already stated, is 760 mm. It is not necessary, of course, that the volumes of gases to be compared should be measured under these conditions in an experiment. The volume of any gas at 0° and 760 mm. can be calculated from the volume measured at any other temperature and pressure by applying Boyle's and Charles's laws.

13. Changes in Volume when Both Pressure and Temperature Change

To derive the general equation that deals with changes in both pressure and temperature we may proceed as follows. Assume that the volume is v_1 at pressure p_1 and temperature (Absolute) T_1 . If the temperature is constant, while the volume changes to v' , and the pressure to p_2 , by Boyle's law

$$p_1 v_1 = p_2 v'.$$

Now let the pressure remain constant, while the temperature changes from T_1 to T_2 . The volume changes, at the same time, from v' to v_2 , and according to Charles's law

$$\frac{v'}{T_1} = \frac{v_2}{T_2} \quad \text{or} \quad v' = \frac{v_2 T_1}{T_2}$$

Now substitute this value of v' in the first (Boyle's law) equation

$$p_1 v_1 = p_2 \times \frac{v_1 T_1}{T_2}$$

If we solve this equation for v_2 , we obtain

$$v_2 = \frac{v_1 T_2 p_1}{T_1 p_2}$$

Let us consider a sample of gas that occupies 200 ml (v_1) at a temperature of 20° C (293° Absolute) and a pressure of 720 mm. What volume (v_2) will this gas occupy at 0° C (273° Absolute) and 760 mm?

$$v_2 = \frac{200 \times 273 \times 720}{293 \times 760}$$

14. Dalton's Law Partial Pressures of Gases in a Mixture

In our previous study of the pressure exerted by a gas, we have assumed that the volume is occupied by a single substance. We must now consider the relation of the pressure of each gas in a mixture to the total pressure and to the relative amount of that gas in the mixture. Let us take one liter of oxygen, measured at a pressure of one atmosphere. Let us next assume that a liter of nitrogen, measured also at one atmosphere, is forced to occupy the same space as the oxygen. We thus compress two liters of gas into a volume of one liter. The total pressure of the mixture of the two gases is found to be two atmospheres, provided that the temperature remains unchanged. Each gas in the mixture occupies the same volume — one liter — and its molecules must exert the same pressure — one atmosphere — as they did before the mixture was made. The principle involved here is of considerable importance.

Dalton's Law of Partial Pressures, which applies to situations of this kind, may be stated as follows: *The total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases that compose the mixture.* The partial pressure of one of the gases of the mixture is proportional,

at a definite temperature and for a constant volume, to the number of molecules of that gas. This pressure is the same as the pressure that the same number of molecules would exert upon the walls of the container, if they alone, at the same temperature, occupied the volume that the mixture occupies. For example, in the mixture of oxygen and nitrogen described above, the partial pressure of oxygen is one atmosphere. This is the same pressure as the same quantity of oxygen would exert if it alone occupied the same volume (1 liter) as the mixture occupies. The partial pressure of nitrogen is also one atmosphere, and the total pressure (two atmospheres) is the sum of the two partial pressures.

Dalton's law can also be stated, perhaps more simply, as follows: Each gas in a mixture exerts the same pressure as it would exert if it alone occupied the whole volume that the mixture occupies, or at least its contribution to the total pressure is equal to this pressure. Thus, the oxygen in one liter of an (at one atmosphere) would exert a pressure of one fifth of an atmosphere, if the oxygen alone occupied the whole liter, at constant temperature. We may also point out that the volume which the oxygen would occupy, if it exerted one atmosphere of pressure, would be one fifth of a liter.

15. The Correction of the Volumes of Gases Measured in the Presence of Water Vapor

The volumes of gases are sometimes measured under conditions that do not exclude, entirely, all other substances. Many gases, for example, are collected over water as shown in Figure 57. Under these conditions, the collecting vessel is filled with a mixture of the gas collected and water vapor. At a definite temperature, water produces a definite quantity of vapor, the exact amount depending upon the extent of the space above the liquid and upon the temperature. At a given temperature this vapor exerts a definite pressure per unit of area on the surface. At any other temperature, the pressure exerted by the vapor is greater, if the temperature is higher, and less, if the temperature is lower. When the vol-

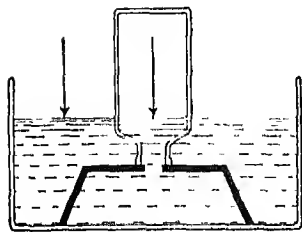


Figure 57. The Collection of a Sample of Oxygen over Water

The gaseous pressure inside the bottle is made up of the partial pressure of oxygen and the partial pressure of water vapor. Together they are equal to the atmospheric pressure.

ume of the gas, which is mixed with water vapor, is measured, a correction must be made for the presence of water vapor. The volume that the gas would occupy, if it were dry, is less than that which it occupies at the same pressure when water vapor is present.

Let us consider an experiment in which 200 ml of oxygen is collected over water at a temperature of 20°C and a pressure of 770 mm. The pressure of 770 mm is the total pressure of water vapor and oxygen. To find the partial pressure exerted by oxygen, the pressure of the water vapor must be subtracted from the total pressure. The pressures of water vapor at different temperatures have been determined by experiment and are given in Table 1 of the Appendix. We find that the partial pressure of water vapor at 20°C is 17.5 mm. Hence, the partial pressure of oxygen (Figure 57) is $770 - 17.5 = 752.5$ mm.

The pressure of 752.5 mm is the pressure that would be exerted upon the walls of the container by the *dry* oxygen if its volume were 200 ml. The volume (v_2) that the dry oxygen would occupy if it exerted a pressure of 770 mm, can be calculated by using Boyle's Law as follows.

$$752.5 \times 200 = 770 \times v_2 \\ v_2 = 195.5 \text{ ml}$$

If we wish to determine the volume (v_s) of dry oxygen under standard conditions, we could set up and solve for the value of v_s in either of the following equations:

$$(1) v_s = \frac{200 \times 752.5 \times 273}{760 \times 293} \text{ ml}$$

$$(2) v_s = \frac{195.5 \times 770 \times 273}{760 \times 293} \text{ ml}$$

16. Diffusion of Gases, Graham's Law

A gas that is liberated in one part of a closed vessel distributes itself — diffuses — throughout the entire space, although one or more other kinds of gas may be already present. The vessel seems never to be filled by gases, there is always room for one more, and all the gases placed in the vessel are, eventually, uniformly mixed. Gases already present do not prevent the diffusion of a gas that may be added, but collisions between molecules do retard diffusion to some extent. Furthermore, diffusion occurs regardless of differences in the densities of the gases in the mixture, the heavier gases diffuse more slowly than the lighter ones, but there is never a complete separation into layers with the heaviest gas at the bottom and the lightest at the top of the container.

The diffusion of gases can be demonstrated by placing a heavy colored gas, such as bromine vapor, in the bottom of a cylinder filled with air and closed with a glass plate. After a time, the brown bromine vapor will be seen to have distributed itself over the entire volume of the cylinder, although bromine is more than five times as dense as air. The presence of air in the container does *retard* the expansion of the bromine vapor. The retarding effect of air can be observed by breaking two bottles containing liquid bromine in two cylinders, one filled with air and the other evacuated. In the latter, bromine vapor fills the cylinder immediately.

Graham, in 1832, measured the rates of diffusion of different gases and from the results of his study formulated the law that bears his name. *The rates of diffusion of gases are inversely proportional to the square roots of their densities.* The density of a gas refers to the weight of one liter of the gas measured, unless otherwise specified, under standard conditions. The weight of any volume can of course be used, if the volume is the same for all gases for which rates of diffusion are to be compared.

Differences in the rates of diffusion of hydrogen,

which is the lightest of all gases, and the oxygen and the nitrogen in the air can be demonstrated by the experiment shown in Figure 58. A porous cylinder (C) is filled with air and connected, by means of a glass tube, with a vessel partially filled with water. A vessel containing hydrogen is lowered over this cylinder. Hydrogen diffuses through the porous walls of the cylinder more rapidly than oxygen and nitrogen diffuse outward, with the result that the pressure increases inside the cylinder and the vessel with which it is connected. Because of the increase in pressure, water is forced through the outlet tube (A).

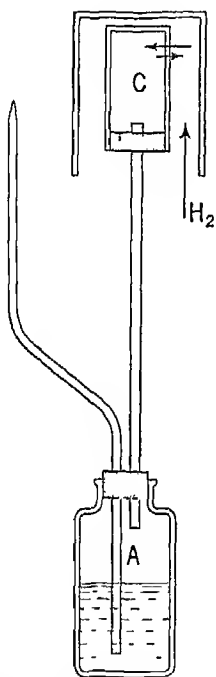


Figure 58 Apparatus Used to Show the Different Rates of Diffusion of Hydrogen and Air

The average density (weight per liter) of air is 1.293 and that of hydrogen is 0.08987, at 0° C and 760 mm. According to Graham's law, therefore, the rates of diffusion of hydrogen and air are related as follows:

$$R_{H_2}/R_{air} = \sqrt{1.293} / \sqrt{0.08987} = 3.8$$

This means that hydrogen diffuses approximately four times as rapidly as air.

THE KINETIC THEORY

17 Introduction

In the preceding pages of this chapter we have become acquainted with many of the general properties of gases.

(1) All gases are easily compressed as compared to liquids and solids.

(2) They diffuse rapidly throughout the entire space of their containers.

(3) One gas can diffuse through space occupied by another.

(4) Mixtures of gases do not settle out into layers.

(5) In a mixture each gas exerts the same pressure as it would if it occupied, alone, the entire volume, and therefore one gas in the mixture does not interfere with the behavior of others.

(6) The volume of a gas varies inversely with the pressure that the gas exerts and directly with the Absolute temperature.

(7) The effect of changes in pressure and temperature upon volume is the same, in general, for all gases.

(8) The rate of diffusion depends upon the density of the gas.

(9) The densities of gases are small as compared to densities of liquids and solids.

(10) A gas exerts pressure in all directions upon the walls of the vessel that contains it.

Most important of all, we have seen that these are *general properties of all gases* and of mixtures of gases. There can be no doubt, therefore, that all gases have the same kind of structure.

18 The Kinetic Theory

With the information that we have before us concerning the behavior of gases, we are now ready to seek an explanation of their structure that will account for their behavior. This explanation must answer many questions. How does a gas exert pressure in an upward direction? Why do gases in a mixture not interfere under ordinary conditions with one another? Why are gases so much more easily compressed than liquids and solids? How can one gas diffuse into the space that another occupies? Why do mixtures of gases not settle out into layers?

As these and similar questions were studied over a long period of time, there gradually emerged a theory that provided satisfying answers to all of them. The principal parts of this theory — The Kinetic Theory of Gases — are summarized below.

(1) Gases are composed of particles, which we now call molecules. As compared with their own dimensions, these molecules are separated by great distances. Between them, there is only empty space.

(2) The molecules are in motion and their velocities depend upon the temperature. They collide with one another and strike the walls of the containing vessel. The pressure that a gas exerts upon the walls of its container is the result of the bombardment of the walls by the molecules.

(3) The molecules are perfectly elastic — they collide with one another and with the walls of their container without loss of energy.

(4) The molecules have very little attraction for one another. Their velocities are sufficiently great to cause them to scatter instead of coalescing to form larger particles, or a more or less compact mass, as they probably do in liquids and solids, in which the molecules are closer together, move more slowly, and therefore exert stronger attraction for one another.

(5) The average kinetic energy of all the different kinds of (gas) molecules at the same temperature is the same, regardless of differences in mass. Since the kinetic energy of a molecule is defined by the equation

$$KE = \frac{1}{2} mv^2,$$

the light molecules of hydrogen, for example, must travel faster than the heavier molecules of oxygen. The former must make up what they lack in mass by increased velocity. According to this point of view, a mixture consisting of a billion particles each of hydrogen and oxygen confined in the same volume would exert a pressure twice as great as the pressure exerted by a billion particles of either gas alone. If the average kinetic energies of hydrogen and oxygen molecules were not the same, the mixture would not exert a pressure equal to twice that of either individual gas.

HOW THE KINETIC THEORY EXPLAINS THE GAS LAWS

19 Boyle's Law

The fact that all gases are extremely compressible can best be explained by the assumption that gases are composed of molecules that are relatively far apart and are separated by empty space. Added pressure crowds the molecules closer together, thereby decreasing the volume by "crowding out" some of the space between the molecules. The kinetic theory assumes that the molecules of a gas actually occupy only a very small part of the volume occupied by the gas as a whole under ordinary pressure conditions. As long as the volume actually occupied by the molecules themselves is not compressed, all gases should respond in the same manner to changes in pressure. This does not mean that individual molecules of two different gases are of the same size and would occupy the same space if we could consider them as single particles. It means that the space occupied by the molecules of any gas is always about the same fraction of the entire volume, regardless of the character of the gas. This condition is possible, of course, because the fraction is very small.

The pressure of a gas is explained by the assumption that the molecules are in rapid motion. Hence, the pressure against the walls of the container is caused by the bombardment of the walls by molecules and is directly proportional to the number of molecules confined within a given volume. Let us consider a definite weight of a gas that occupies two liters at a temperature that is not changed. If the same number of molecules is crowded into one liter, Boyle's law predicts that the pressure will be twice as great as when the volume is two liters. The kinetic theory explains the increase in pressure as follows. When the molecules are crowded into one half the volume that they first occupied, there are twice as many impacts upon the same area of wall surface as

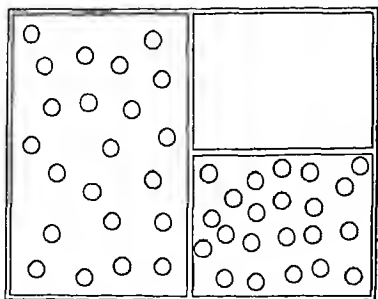


Figure 59 An Explanation of Boyle's Law

The same number of molecules will exert twice as much pressure per unit of surface when they are crowded into one half of the original volume

before. The increased number of impacts results in twice as much pressure.

20 Charles's Law

According to the kinetic theory, the pressure of a gas upon the walls of its container depends upon the bombardment of the walls by the molecules and is determined (1) by the number of molecules in a definite volume, (2) by the mass of one molecule, and (3) by the average velocity with which the molecules move. These conditions determine the number of impacts between walls and molecules that will occur in a certain period of time and also the pressure that will result from the impacts, since the pressure produced is proportional to the *momentum*, which for one molecule is equal to its mass times its velocity.

How can we explain the increase in pressure as the temperature is raised? The answer is fairly simple. The rise in temperature cannot affect either the number of molecules or their masses; it must, therefore, increase the velocities of the molecules. If the molecules move more rapidly at the higher temperature, not only will more of them strike a definite area of surface, but each molecule will possess greater momentum, and each impact will result in greater pressure. A bullet shot from a gun will produce more effect when it strikes a steel plate than one of equal mass that is thrown, with smaller velocity, by the hand. Thus we

should naturally expect direct relation between changes in temperature and changes in the pressure of a gas at constant volume; or if the volume changes and the pressure remains constant, a similar direct relation should be expected between the volume and the temperature.

21. Dalton's Law

The behavior of gases in mixtures indicates that each gas acts independently of the others, each gas exerts the same pressure as it would if it were present alone in the container. The kinetic theory explains this fact. If each gas is composed of particles that are widely separated, with empty space between and around them, the particles of one gas in a mixture may easily find plenty of free space that is not occupied by particles of other gases. Each kind of molecule strikes the walls just as often, and therefore exerts just as much pressure, as it would if other molecules were not present.

Under high pressure, when molecules are crowded closely together, Dalton's law does not hold. We should not expect it to hold under these conditions, because a molecule in a crowded space cannot move as freely as it can in a free and uncrowded space. When molecules are crowded, they do interfere with one another, and the number of each kind of molecule that can strike the walls in a given period of time is reduced. The situation is much the same as that of a person who tries to reach his destination in a crowded street as compared with another who covers the same distance when the street is deserted.

22 Other Causes of Deviations from Dalton's Law

If the molecules of different gases in a mixture react to form new molecules, there may be, and frequently is, a change in the total number of molecules. When this happens, the pressure is equal to the sum of the partial pressures of all the parts of the mixture — the original gases that remain unchanged and the new substances formed.

by the reaction. Accordingly, we should not expect the total pressure of the mixture, at constant temperature and volume, to be equal to the sum of the partial pressures of the gases that were mixed. Even if the gases of the mixture do not react, their molecules may have stronger attraction for one another than they have for molecules of their own kind. This attraction should affect the velocities of the molecules, and therefore it should also affect the pressures that they can produce. When any of these conditions prevail, Dalton's law cannot be applied accurately to mixtures of gases.

23. Diffusion

We cannot explain the expansion and diffusion of gases without using certain parts of the kinetic theory. It might be said, of course, as it was said at one time, that a gas expands from a region of high pressure into one of low pressure, because "nature abhors a vacuum," but a statement of this kind explains nothing. It is not a good theory or even a good guess, because it offers no basis for understanding the diffusion of gases into space already occupied by other gases and where, therefore, a vacuum does not exist. Nor does this "answer" to the problem explain why nature should try to fill a vacuum with gas or the conditions under which a vacuum can be said to be filled.

If gases are composed of molecules in rapid motion and separated by relatively great distances, as the kinetic theory assumes, then the space occupied by one gas can be penetrated by the molecules of another. The theory also explains why gases

of small density diffuse more rapidly than heavier ones. One of the principal statements in the theory assumes that the molecules of different gases, regardless of their masses, possess the same average kinetic energy at the same temperature. Since the kinetic energy of a molecule is defined as $\frac{1}{2}mv^2$, and if the kinetic energy for all molecules is the same, then those molecules that have the larger masses must have the smaller velocities. The rates of diffusion must depend upon the velocities of the molecules, if they did not move at all, there could be no diffusion. Hence, it follows that the rate of diffusion of a gas is slower, the greater the mass of its molecules, or the greater the density of the gas.

24 Derivation of the Equation for Graham's Law

The mathematical statement of Graham's law (page 95) can be derived by applying the principle in the kinetic theory which states that the average kinetic energies of the molecules of two gases are the same at the same temperature. Consider two gases, the molecules of which have masses of m_1 and m_2 and velocities of v_1 and v_2 , respectively. Then

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

Dividing both sides of this equation by $\frac{1}{2} m_1 v_2^2$, we obtain

$$\frac{v_1^2}{v_2^2} = \frac{m_2}{m_1} \quad \text{or} \quad \frac{v_1}{v_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}}.$$

This equation now shows that the velocities of the two molecules (rates of diffusion depend directly upon the velocities) are inversely proportional to the square roots of their masses. The masses of the molecules are in the same ratio as the gram-molecular weights (page 44) of the gases, and the gram-molecular weights are the weights of equal volumes (22.4 liters) of the two gases under standard conditions (page 91). Density is defined as the weight per unit of volume ($d = m/v$). Hence,

$$\frac{v_1}{v_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$

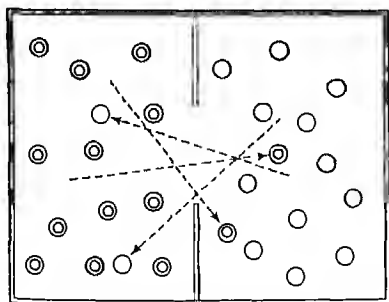


Figure 60 An Explanation of How One Gas can Diffuse into the Space Occupied by Another

25 Gases Do Not Settle

The molecules of different gases do not settle out in layers from a mixture, they remain more or less permanently mixed. If a gas of small density is mixed with one of relatively great density, some slight separation naturally results, because of the slower velocity of the heavier molecules, to observe such changes, however, a very long vertical column of the mixture must be examined. Thus, the percentage of carbon dioxide in the air near the surface of the earth is small (0.035 per cent), and at higher levels of the atmosphere the percentage is even less, and finally becomes zero. This condition is the result, in part, of the density of carbon dioxide (1.95) as compared with that of the other components of the air, the average density of which (weight per liter at 0° and 760 mm) is 1.293. The percentage of hydrogen (density 0.08987) increases with the altitude. There are no levels, however, at which the different components of the air settle out in layers; the change in composition varies gradually with the elevation. This variation in composition is, in itself, good evidence that air is a mixture of several kinds of *particles*. The failure to separate into layers is explained satisfactorily if each gas is composed of molecules that are moving in all directions and therefore tend to remain scattered.

A gas does not settle to the bottom of its container. The moving molecules, therefore, must suffer no loss of (average) energy when they collide with one another or strike the walls of their container. As a result of a single collision, one molecule may lose energy, and another may gain energy, but over a long period of time the average energy of each molecule remains unchanged at constant temperature, in some collisions a molecule gains energy, and in some it loses. The kinetic theory includes, therefore, the principle that molecules of gases, in collisions, are *perfectly elastic*. If they suffered a loss of energy (were inelastic) when they collided,

they would lose velocity, and eventually they would cease to move at all, except to settle out under the influence of gravitation.

26 Deviations from the Gas Laws

All gases can be liquefied by cooling and by the application of pressure. Near the temperature and pressure at which a gas condenses to form a liquid, we should expect the gas laws to apply less generally and accurately than at higher temperatures. In other words, we should expect that a gas at a temperature and pressure only slightly different from the conditions under which it changes to a liquid would display properties somewhat like those of a liquid. The essential differences in the properties of the liquid and gaseous states appear to arise from differences in the distances that separate the molecules and from differences in the attraction that molecules exert upon one another. There is also a difference in energy content, since energy is released or absorbed when one state is changed into another. Molecules of liquids are more closely and firmly held together by the forces of attraction that produce cohesion; molecules of gases cohere only slightly because of the relatively great distances between them. As the conditions of a gas are altered so that they approach more nearly the conditions under which the gas becomes a liquid, the laws that apply to the gaseous state are less and less valid. Finally, when the gas is liquefied, they are no longer valid in any sense.

We must recognize, however, that even in gases there is some attraction of molecules for one another and that this attraction results, to a slight extent, in cohesion. When the temperature is relatively high, and when the molecules are not crowded closely together by relatively great pressures, the forces that produce cohesion are not great, although they do exist. It is well known, for example, that Boyle's law does not hold exactly. Upon first thought, one might regard

this failure as a cause for serious doubt of the validity of the kinetic theory, but second thought will show that the failure is predicted by the theory itself. If two liters of oxygen (one atmosphere) are compressed by doubling the pressure, the new volume is 0.999 liter, instead of one liter, the volume that Boyle's law would lead one to expect. The increase in the external pressure, caused by changes from without, compresses the gas to one liter, but it appears that there is an additional pressure of some kind that causes a further reduction of the volume amounting to 0.001 of a liter, or one milliliter. This additional pressure is the effect of the increased attraction of the molecules for one another when they are crowded closer together. This attraction has the same effect as an increase in the external pressure; it tends to draw the molecules still more closely together and causes a slightly greater decrease in volume than corresponds to the increase in pressure. At low temperatures, molecules move more slowly and offer less resistance to cohesion and therefore, the compression caused by molecular attraction becomes more pronounced. For the same reasons, the lower the temperature, the more easily a gas is liquefied.

The molecular attraction is also much greater for some gases than for others, it is greatest in those gases which are most easily liquefied. As a matter of fact, condensation of the gas to a liquid occurs at the temperature at which the kinetic energy of the molecules becomes insufficient to counteract the attraction that causes them to be drawn together and that produces the cohesion characteristic of the liquid state of the substance at that temperature. The attraction between the molecules of some gases is stronger than the attraction between the molecules of other gases. Hence the reduction in the kinetic energy of some kinds of molecules must be greater than for others before the cohesion of the liquid state can result.

Let us consider another deviation from Boyle's law. When gases already highly compressed are subjected to further increases

in pressure, their volumes are not diminished as much as Boyle's law would lead one to predict. The compression of gases under ordinary conditions reduces the volume by crowding the molecules closer together; the reduction in volume is really a reduction in the amount of empty space. When the pressure is very high, the molecules are already crowded so closely together that the volume which they actually occupy is a large part of the whole volume of the gas. Since the volumes of the molecules themselves are not compressed, only a slight fraction of the whole volume can be affected by an increase in pressure in the manner predicted by Boyle's law, the whole volume is not inversely proportional to the pressure. The deviation from the law, from this cause, may be considerable under pressures of two hundred atmospheres or more. Thus, one liter of hydrogen at room temperature and one atmosphere becomes, not 0.005, but 0.00555 liter when the pressure is increased to two hundred atmospheres at the same temperature.

For satisfactory interpretations of these deviations from the gas laws the fundamental assumptions of the kinetic theory are just as necessary as they are for the interpretation of the laws themselves. Strictly speaking, the laws apply only to gases whose molecules have no attraction for one another, which therefore do not cohere, and which occupy no part of the whole volume. Since there are no gases of this kind, we can speak of them only as *ideal* or *perfect* gases. Under the ordinary conditions of measuring the temperature, pressure, and volume of a gas, the deviations are so slight that the laws may be applied without corrections. These corrections can be made if the errors are sufficiently great to demand consideration.

27 The Liquefaction of Gases

All gases can be liquefied under the proper conditions of temperature and pressure. For a given pressure — let us say that this is one atmosphere — there is a definite tem-

perature at which the liquid boils. At the same temperature, pressure remaining constant, the gaseous state of the substance may be condensed to form the liquid. The liquid boils at a lower temperature if the pressure is reduced. Thus, water boils at 100°C when the pressure is one atmosphere, and at about 65° when the pressure is reduced to 200 mm. Raising the temperature and reducing the pressure therefore aid in the production of the gaseous state. On the other hand, cooling and increase of pressure aid in the liquefaction of a gas.

If we are to convert a gas into a liquid, we must increase the attraction of the molecules for one another, and we must slow them down so that they will no longer have sufficient energy to overcome the forces that bind them together. The first of these conditions is accomplished by crowding the molecules together — by increasing the pressure. The second is accomplished by cooling, since the velocities of the molecules decrease as the temperature falls.

Sometimes, cooling without an increase of pressure results in the liquefaction of the gas. This is true, for example, of the condensation of water vapor. If the boiling point of the liquid is very low, the gas must be cooled to an extremely low temperature (-183° in the case of oxygen and -252.7° in the case of hydrogen) before it can be liquefied without changing the pressure. For such gases it is much more practical to aid liquefaction by using increased pressure. Thus, oxygen can be liquefied at -118° , if a pressure of about 50 atmospheres is applied. Carbon dioxide can be liquefied at 0° , when a pressure of 38 atmospheres is applied, at 30° , 71 atmospheres must be used; and above 31.1° , it cannot be liquefied, regardless of the pressure that is applied.

28 Critical Temperature

The temperature above which a gas cannot be liquefied by any pressure is called the *critical temperature* of that gas. Above this temperature, the substance can exist only in

the gaseous state. The pressure required to liquefy a gas at the critical temperature is the *critical pressure*. Thus, the critical pressure of carbon dioxide is 71 atmospheres.

TABLE 4
CRITICAL TEMPERATURES OF GASES

Gas	Boiling Point, $^{\circ}\text{C}$ (1 atmosphere)	Critical Temperature $^{\circ}\text{C}$.
Hydrogen	- 252.7	- 239.9
Nitrogen	- 196	- 147.1
Oxygen	- 183	- 118.8
Carbon dioxide	Sublimes	31.1
Ammonia	- 33.3	132.4
Sulfur dioxide	- 10	157.2
Water	100	374

SUMMARY

<i>Properties of gases</i>	<i>Interpretations in terms of the kinetic theory</i>
Compressibility	Molecules are separated by empty space. When gases are compressed, the molecules are crowded closer together. The amount of empty space between the molecules is reduced.
Pressure	The pressure of a gas is caused by the bombardment of the walls by the molecules. The pressure which the gas exerts depends upon the number of molecules which strike a definite amount of surface at a given instant and upon the velocity and mass of the molecules. The average kinetic energy of all kinds of (gaseous) molecules is the same. Hence the heavier molecules must have smaller velocities.
Boyle's Law: Effect of Pressure upon Volume	In dilute gases the molecules are far apart and cohere only slightly. If the same number of molecules are crowded into one half the original volume, twice as many will strike a defi-

nite surface on the walls at a given instant. Hence the pressure exerted will be twice as great. In more concentrated states Boyle's law does not hold because a large part of the space is filled by the molecules themselves. There is less empty space to be compressed.

Charles's Law
Effect of
Temperature
upon Volume
or Pressure

The molecules move more rapidly as the temperature increases. The increase in velocity causes a gas to exert a greater pressure at constant volume or to occupy a larger volume if the pressure remains constant.

Dalton's Law of
Partial Pressures

The molecules of gases in a mixture, under low pressures, are far enough apart so that they do not interfere with one another. Each gas therefore exerts the same pressure as it would exert, in the same volume, if the other gases were not present.

Diffusion

The molecules are in rapid motion and are far apart. Due to the porous character of a gas, it is possible for one gas to diffuse into the space already occupied by another. The molecules of one gas move through the empty space between the molecules of the other. The velocities of the molecules are inversely proportional to the square roots of their masses.

Gases do not
settle

Molecules are perfectly elastic.

Deviations from
gas laws

Molecules of gases possess some attraction for one another and at high pressure and low temperatures are separated by less empty space than under ordinary

conditions. A gas already under high pressure does not obey Boyle's law, because most of the empty space has already been crowded out, and added pressure no longer means that the molecules are simply crowded closer together.

All gases can be
liquefied

In a gas the molecules are separated because they are moving. In a liquid they are close together and strongly attract one another. Cooling slows down the molecules. Pressure crowds them closer together. Hence cooling and increased pressure aid in liquefying a gas, because they both tend to produce the molecular state of the liquid.

Review Exercises

- 1 The volume of a sample of gas at 20°C is 280 ml. What will be its volume if the temperature is reduced to -250°C ?
- 2 A sample of gas measured at 22°C and 740 mm occupies 200 ml, and weighs 0.21 g. What is the weight of a liter of the same gas measured under standard conditions?
- 3 A mixture of two gases, *A* and *B*, exerts a pressure of 700 mm and occupies 500 ml. If the pressure of gas *A* alone is 200 mm, under the same conditions of temperature and volume, what fraction of the whole volume would each gas in the mixture occupy, alone, at a pressure of 700 mm?
- 4 One liter of a gas measured at 0°C weighs 2.42 g. What will one liter of the same gas weigh if measured at 273°C , the pressure remaining unchanged?
- 5 The volume of a sample of oxygen, measured over water at 30°C and 738 mm, is 468 ml. What would be the volume of the sample if it were dry and were measured under standard conditions?
- 6 Ten liters of air at 0°C are brought into a room where the temperature is raised to 25°C . What pressure would have to be ex-

- erted on the air to prevent a change in volume if the original pressure was 760 mm?
- 7 Sulfur dioxide is approximately 32 times and carbon dioxide is approximately 22 times as heavy as hydrogen, liter for liter. Compare the rates of diffusion of sulfur dioxide and carbon dioxide.
 - 8 In terms of the kinetic theory explain the following features of the behavior of gases (1) diffusion, (2) compressibility, (3) effect of temperature upon pressure at constant volume and upon volume at constant pressure.
 - 9 How do cooling and increase of pressure aid in the liquefaction of gases?
 - 10 Enumerate the differences in behavior of gases and liquids. How are these differences explained?
 - 11 What evidence indicates that the average kinetic energies of all kinds of molecules in the gaseous state are the same at the same temperature?
 - 12 What evidence indicates that the molecules of a gas are perfectly elastic?
 - 13 Describe the properties and physical conditions of a "perfect" gas.
 - 14 Why do gases not obey Boyle's law exactly (1) under ordinary pressures and (2) under very high pressures?
 - 15 What are some of the indications that molecules of a gas are (1) moving, (2) far apart, and (3) have relatively slight attraction for one another?
 - 16 What conditions of atmospheric pressure prevail in a region indicated on a weather map as a cyclone? What is the general direction of movement of cyclones in the United States? What kind of weather usually accompanies a cyclone? What is the difference between a cyclone and a hurricane or tornado? (Consult some reference on meteorology, or an encyclopedia.)
 - 17 What conditions cause the atmospheric pressure to vary from day to day at one place on the earth's surface?
 - 18 What would be the effect of subjecting ammonia at 140°C to gradually increasing pressure? Compare with the effect at 50°C .
 - 19 A and B are directly proportional, C and D are inversely proportional. Explain these two statements.
 - 20 Describe the measurements and calculations that would be necessary in order to compare the weights of equal volumes of two gases.
 - 21 The density of a gas is 1.5. What further information must be given, or understood, about this statement before it can be regarded as having much meaning or value?
 - 22 The pressure of a mixture of gases A and B is 400 mm, when the volume is 400 ml. If the partial pressure of A is 100 mm, what volume would the quantity of A that is present in the mixture occupy if its pressure were 400 mm and B were not present? If its pressure, when alone, were 100 mm?
 - 23 If all of the air in a room 15 by 9 by 20 feet and at a pressure of 760 mm were compressed until the volume became 1 cu. ft., what pressure would it exert, temperature remaining constant?

References for Further Reading

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HYDROGEN

By placing a saucer of white porcelain in a jet of inflammable gas burning tranquilly at an orifice, I found that the part of the saucer which the flame licked was moistened by small drops of liquid as clear as water, and which, in fact, appeared to be nothing but pure water

MACQUER (1776)

1. Introduction

This chapter deals with the history, occurrences, methods of preparation, properties, and uses of hydrogen. In addition, it introduces two other topics of considerable importance: (1) the differences in activity of the metals and the table in which they are arranged to show these differences, and (2) a reversible reaction.

2. History

The discovery of hydrogen is usually credited to Henry Cavendish who, in 1766, prepared it by the action of acids upon certain metals and by the action of steam upon iron. The action between metals and acids had been observed many times by the alchemists, but the gas produced by these reactions was thought to be a special kind of air. In fact, air was the only gas known at that time. Paracelsus, for example, some time in the early part of the sixteenth century, treated iron with sulfuric acid and observed the "air" that was evolved. He described this "air" as arising from the mixture and "bursting forth like a wind." In the eighteenth century, hydrogen was prepared by the same methods and was identified with phlogiston, the substance that was thought to escape from substances during combustion. It was observed that the "air" pre-

pared by the action of sulfuric acid upon iron and other metals reacted with the calx (or ash) resulting from the combustion or corrosion of the metals in air and changed them into metals again. We should describe this change today as a reaction in which the hydrogen reduces the oxides of the metals, i.e., hydrogen combines with the oxygen of the oxide (calx) and leaves the free metal; but the earlier interpretation of this action of hydrogen inclined to the view that phlogiston re-entered the substances from which it escaped during combustion.

Hydrogen was called "inflammable air," a name suggested by Cavendish, who recognized the gas that he prepared as an independent substance, different in many respects from other kinds of "air." Probably because of the prevailing opinion that all gaseous materials must be different varieties of air, Cavendish did not realize that he had prepared an element. Lavoisier showed that Cavendish's "inflammable air" is a constituent of water and that it is an element. He suggested the name *hydrogen*, which signifies "water former," for the new element.

3 Occurrence

Unlike oxygen, hydrogen is seldom found free in nature, at least not on the earth or in the atmosphere near the earth. The gases

escaping from volcanoes contain small amounts; and some hydrogen, 0.5 per cent or less, occurs in natural gas. Only minute traces—one part, by volume, in 10,000—are found in the atmosphere near the earth's surface. The quantity increases with altitude, until at eighty miles above the earth whatever atmosphere there may be at that altitude is probably composed very largely of hydrogen. This element also appears in the sun and in many of the stars. At the time of an eclipse, long streamers of flaming hydrogen can be observed around the sun, extending from the sun's atmosphere one hundred thousand miles or more into space.

In the combined state hydrogen is relatively abundant, although it accounts for only about one per cent of the weight of the earth's crust. The small percentage (by weight) of hydrogen is explained by the very small mass of the hydrogen atom; probably there are more atoms of hydrogen in the crust of the earth than of any other element with the exception of oxygen. Water contains approximately one gram of hydrogen for every eight grams of oxygen. Hydrogen is found in combination with carbon in natural gas, in petroleum, and in products obtained from petroleum, such as gasoline, kerosene, and motor oils. In addition to these occurrences, hydrogen is found in combination with carbon, oxygen, and a few other elements in substances produced by, or associated with, living things; cellulose ($C_6H_{10}O_5$) and sucrose or sugar ($C_{12}H_{22}O_{11}$) are examples of such compounds. It is present in all the tissues of our bodies and in all our foods. In organic compounds, it is almost as important as carbon, and consequently is found in almost all fats, oils, alcohols, proteins, soaps, dyes, drugs, explosives, perfumes, and flavors. Hydrogen is also present in acids and in hydroxides (bases).

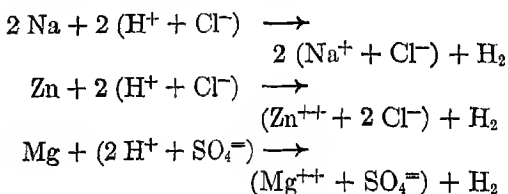
THE PRODUCTION OF HYDROGEN

The methods of producing free hydrogen, like those of producing oxygen, can be

classified as (1) laboratory methods and (2) industrial methods. The former, in general, are simpler than the latter but employ materials that are not economical industrial sources of the element. We shall first consider laboratory methods that can be used to produce small samples of hydrogen for experimental use.

4. Production of Hydrogen by the Action of Acids and Metals

All acids contain hydrogen, and from some of them hydrogen is liberated by the action of certain metals. Typical reactions of this kind are shown by the following equations:



The only actual reaction occurring in these mixtures is the reaction between the metal and the hydrogen ions:

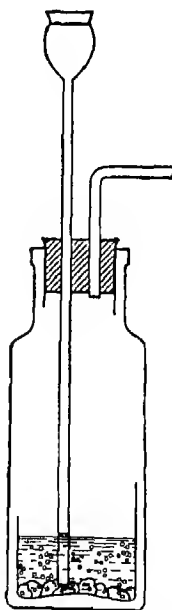
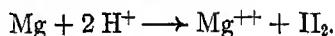


Figure 61 A Hydrogen Generator

The negative ions from the acids (Cl^- or SO_4^{2-}) are not actually involved and can be omitted from the equation. Zinc and hydrochloric acid are the materials most often used.

Only certain acids can be used. Some fail to react noticeably with the metals, while others react to give products other than hydrogen. Nitric acid reacts with many metals, but instead of giving hydrogen, forms water and one or more oxides of nitrogen. The metals that are the most active in liberating hydrogen from an acid, such as hydrochloric, are also the most active in combining with oxygen to form oxides and with chlorine to form chlorides. The most active common metals are sodium, potassium, and calcium. Magnesium is slightly less active than these. Aluminum, zinc, and iron are

very slowly. The least active metals, such as gold, copper, mercury, silver, and platinum, do not displace hydrogen from acids.

In the displacement of hydrogen from an acid by a metal, the hydrogen ions of the acid remove electrons from the atoms of the metal and are converted into neutral atoms. The atoms of the metal, having lost one or more electrons, are converted into positively charged ions.

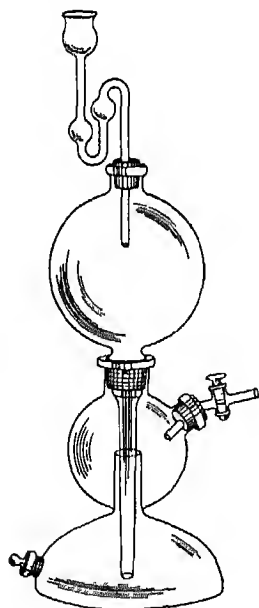
5. The Activity Series of the Metals

The metals may be arranged in an activity series, in which the positions of the metals are determined (1) by the rate at which they cause the evolution of hydrogen from acids, (2) by the activity that they display in combining with oxygen and other elements, or (3) by their displacement of other metals from their compounds. Hydrogen itself may be placed in this series. The metal above hydrogen will displace it from acids; those below hydrogen in the series will not.

ACTIVITY SERIES OF SOME OF THE COMMON METALS

1 Potassium	8. Tin
2 Sodium	9 Lead
3 Calcium	10 Hydrogen
4 Magnesium	11 Copper
5 Aluminum	12 Mercury
6 Zinc	13 Silver
7 Iron	14 Gold

This list of elements, when expanded to include other metals and non-metals, is called the *electrochemical series*, and the use of certain metals in electrochemical cells and batteries depends upon properties that also determine the positions of the elements in the series. Any metal in this list will displace a metal that lies below it from solutions containing ions of the lower metal, conversely, any metal is displaced from solutions of its ions by a metal that lies above it in the series. Thus, iron displaces copper from a solution containing cupric chloride.

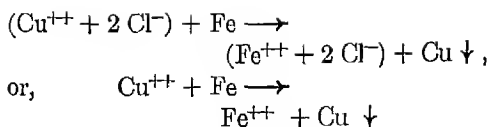


(Courtesy of Arthur H. Thomas Company)

Figure 62 A Kipp Generator

A metal, usually zinc, is placed in the middle compartment. Dilute hydrochloric acid is added through the thistle tube at the top.

still less active, but all of these metals cause a rapid evolution of hydrogen from such acids as hydrochloric or sulfuric. Still other metals, such as nickel and tin, liberate hydro-

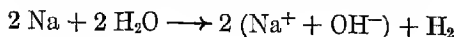


In this reaction, the atom of iron gives two electrons to the cupric ion, thus changing it to a neutral atom of copper. By losing the electrons, the iron atom becomes an ion, Fe^{++} .

With the same metal some acids react to liberate hydrogen more rapidly than others. These differences are caused by the relative ease or difficulty with which hydrogen can be displaced from the molecules of different acids. In other words, they denote differences in the availability of the hydrogen of different acids for reactions with other substances. The availability of this hydrogen is, in a general sense, a measure of the *strength* of the acid. Thus, acetic acid acts slowly with magnesium and must therefore be a relatively weak acid. Hydrochloric acid, on the other hand, reacts much more readily and is therefore relatively strong. Some acids do not liberate hydrogen when they react with any metals. Instead, other products are formed. Thus, when zinc is placed in concentrated nitric acid (HNO_3), the products of the reaction are zinc nitrate, water, and an oxide of nitrogen, NO_2 . Instead of being liberated as the free element in this reaction, hydrogen is oxidized and appears among the products of the reaction as water. The oxygen required for this oxidation is provided by a part of the nitric acid.

6. Production of Hydrogen by the Action of Metals and Water

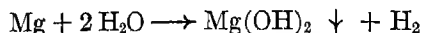
The metals at the top of the activity series violently decompose cold water. When sodium, for example, is placed in water, sufficient heat may be generated to cause the ignition of the hydrogen which is liberated.



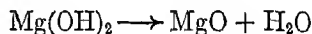
In order to take advantage of the activity of sodium in liberating hydrogen and at the same time slowing the reaction so that it can be controlled, an alloy of sodium with lead or mercury is sometimes used. The effect of the inactive metal upon the activity of

sodium resembles the diluting effect of nitrogen upon the activity of the oxygen in the air. Pure hydrogen is sometimes prepared in small quantities by the use of an alloy of sodium and lead.

Magnesium liberates hydrogen from water only if the water is hot; at least, with cold water the speed of the reaction is scarcely noticeable. The reaction of magnesium with water occurs most readily if a small amount of some magnesium salt is present in the water.

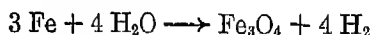


If the magnesium is heated rather strongly and steam is passed over it, a vigorous reaction occurs with the liberation of large quantities of energy as heat and light. Owing to the temperature attained, the oxide of magnesium rather than the hydroxide is formed.



7. The Reaction of Iron and Steam

When steam is passed over iron that has been heated to redness, hydrogen is produced by the following reaction.



The iron must be heated while the reaction is going on, and if the source of heat is withdrawn, the evolution of hydrogen apparently ceases. If the iron is not heated, it is soon cooled by the steam to about 100° , and at this temperature the production of hydrogen is extremely slow. Since iron and steam are relatively easy and cheap to obtain, this reaction is used as one source of the hydrogen required by industry.

8. A Reversible Reaction

The reaction between iron and steam may occur in either direction. Acting in one direction, the reaction produces hydrogen and magnetic iron oxide, Fe_3O_4 . The reverse reaction may be made to occur by passing hydrogen over heated magnetic oxide; this reaction converts hydrogen and the oxide of iron into water and iron. Since they

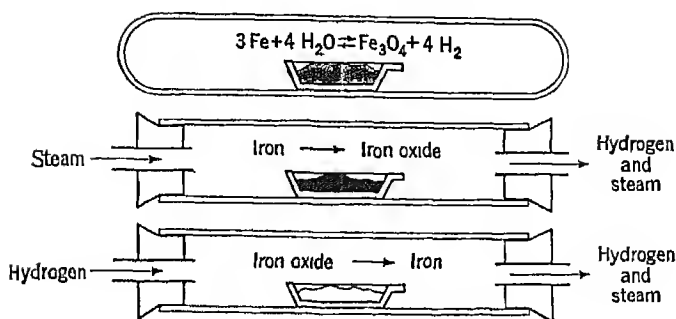


Figure 63 A Reversible Reaction

The reaction is shown (above) as it occurs in a closed tube, as it occurs in the presence of a constant flow of steam (middle), and a constant flow of hydrogen (bottom)

may occur in either direction — the products may react to form the original substances — reactions of this kind are said to be reversible.

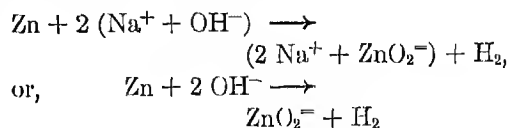
Under the conditions that we have described, however, only one of the two possible reactions occurs. When steam is passed over iron in an open tube (Figure 63), iron can be converted completely into the oxide, provided sufficient time is allowed. The reverse reaction between oxide and hydrogen does not have an opportunity to occur, because the hydrogen is swept out of the reaction chamber and away from the oxide, as rapidly as it is produced, by the constant flow of steam through the tube. Under this condition, the forward reaction may be said to be complete. When hydrogen is passed through the tube and over the oxide, the reverse reaction is complete, and the forward reaction does not have a chance to occur, the steam resulting from the reaction of hydrogen with the oxide is swept out by the constant flow of hydrogen through the tube. If iron and steam are placed in a closed tube and the mixture is heated, neither the steam nor the hydrogen has an opportunity to escape. When the tube is opened, all four substances will be present. We assume, therefore, that both reactions occur when none of the substances involved is removed or is allowed to escape. The two reactions reach a state of *equilibrium*, in which iron and steam react and are consumed at the same rate as they are formed by the reverse reaction. Equilibrium is attained only when none of the substances involved in a reaction is removed from the others.

For some reactions, equilibrium is reached when only relatively small quantities of the products have been formed, others do not attain equi-

librium until most of the original substances have been changed into the products. The conditions that determine the extent to which a reaction occurs before it attains equilibrium, the conditions that disturb equilibrium and cause changes in the composition of the mixture, and the conditions that influence the time required for reactions to reach the equilibrium state, are often of great significance. These subjects are discussed in Chapter 28.

9 Production of Hydrogen by the Reaction of Certain Elements and the Hydroxides of Active Metals

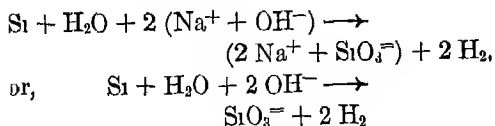
Hydroxides contain the group of atoms, OH, from which hydrogen is displaced by certain elements. This reaction may be demonstrated by warming a solution of sodium hydroxide, NaOH, to which finely divided zinc has been added.



In this reaction the zinc atom replaces two atoms of hydrogen. The compound resulting is called *sodium zincate*, and its formula is usually written as Na_2ZnO_2 . The zincate (ZnO_2^-) group of atoms is similar to the sulfate (SO_4^-) group in sulfuric acid and in sulfates, such as sodium sulfate, Na_2SO_4 .

The reaction of the non-metal, silicon, and sodium hydroxide is of a similar character. To furnish the hydrogen required for the m-

flation of balloons used in military operations, an alloy of iron and silicon, called *ferrosilicon*, is used with a 20 per cent solution of sodium hydroxide



The compound, Na_2SiO_3 , is *sodium silicate* or "water glass"

The similarity of the reactions of zinc and silicon, a non-metal, indicates that zinc, too, reacts as a non-metal with sodium hydroxide. We have previously noted (page 25) that certain elements sometimes act as metals and sometimes as non-metals. The fact that it appears in the ion ZnO_2^{2-} in the same role that non-metals occupy in similar ions, such as SO_4^{2-} , CO_3^{2-} , NO_3^- , and ClO_3^- , is an indication of the non-metallic character of zinc. As a metal, zinc forms compounds such as ZnCl_2 .

COMMERCIAL PRODUCTION

10. Electrolysis

Some hydrogen for commercial uses is obtained as a by-product of the electrolysis of an aqueous solution of sodium chloride (salt). This process is used primarily to produce chlorine and sodium hydroxide and will be discussed at greater length when these substances are considered. Hydrogen and oxygen are also produced by the electrolysis of an aqueous solution of sodium hydroxide (page 66).

11 Explanation of the Electrolysis of a Solution of Sodium Hydroxide

Let us assume that the direct current of electricity used to electrolyze an aqueous solution of sodium hydroxide is supplied by a storage battery, whose poles (or terminals) are connected to wires or strips of metal in contact with the solution (Figure 64). These wires or strips of metal are called the *electrodes* of the cell. The electrode connected to the negative pole of the battery is called the *cathode*, and the one attached to the positive pole is called the *anode*. As a result of

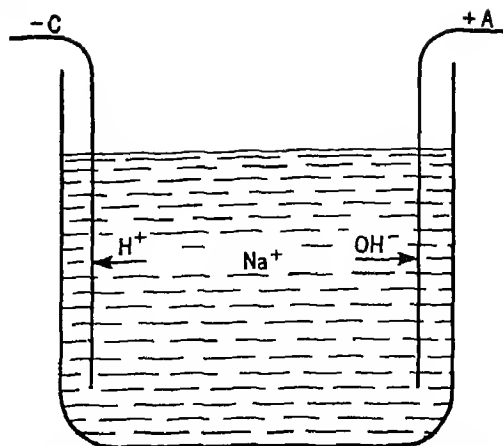
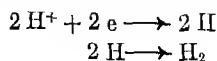


Figure 64 Electrolysis of an Aqueous Solution of Sodium Hydroxide
C, cathode, A, anode

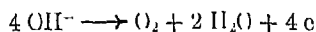
chemical changes occurring in the battery, the number of electrons on the negative pole of the battery, and hence on the cathode of the electrolytic cell, is increased. At the same time, the changes in the battery remove electrons from the anode. There is thus produced a difference in the distribution of electrons in the two parts of the cell, that is, a difference of electric potential between the cathode and the anode. In order to restore the normal, equal distribution of electrons throughout the system, the cathode tends to lose electrons and the anode to gain them. Thus, if a wire is used to connect the two electrodes, electrons will flow through the wire from cathode to anode. In the absence of a wire to channel the flow, the cathode may be expected to yield electrons easily to anything that can accept them — to a positively charged ion, for example. The anode, on the other hand, will remove electrons from anything, such as a negatively charged ion, that can supply them.

The aqueous solution of sodium hydroxide contains sodium (Na^+) and hydroxyl (OH^-) ions from the sodium hydroxide. Water, which produces a relatively small number of ions, supplies some hydroxyl and hydrogen (H^+) ions. The sodium and hydrogen ions, both of which carry a positive charge, migrate toward the cathode, where the hydrogen ions remove one electron each and are converted first into neutral atoms and then into molecules of the element.



Since hydrogen is not very soluble, bubbles of the gas collect on the cathode and then escape into the air if no means is used to collect the gas as it is liberated. Sodium ions are not discharged, because a greater difference of potential is required to convert sodium ions into the free element than is required to discharge hydrogen ions. Even if sodium were liberated, it would in turn react with water (page 108) to form hydrogen and sodium hydroxide.

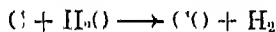
The reaction at the anode probably involves the conversion of hydroxyl ions into oxygen and water



The electrons of the ions are removed by the anode. The reactions that occur at the electrodes result, therefore, in the conversion of the water of the solution into hydrogen and oxygen.

12. Water Gas

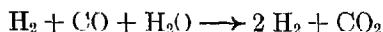
When steam is passed over hot coke (1000°C), the following reaction occurs



Both of the products of this reaction are gases and both are combustible. The first, carbon monoxide, burns to form carbon dioxide, and the second forms water. The mixture of carbon monoxide and hydrogen is called "water gas" and is an important fuel. In practice, the coke is heated by means of an air blast which causes some of it to burn. The heat which is liberated raises the temperature of the remainder of the coke to about 1000°C . Steam is then turned on and the reaction which forms "water gas" takes place. Since the reaction requires heat, the coke is soon cooled below the required temperature. The steam is then cut off, and the mass is reheated by another blast of air, thus preparing it for further reaction with steam.

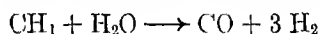
If "water gas" is to be used as a source of pure hydrogen, carbon monoxide must be removed. The mixture of gases is passed, with steam, over a catalytic mass, which consists of the oxides of certain metals (oxides of iron, chromium, and thorium are

used), at a moderately high temperature (about 500°). Under these conditions the steam oxidizes carbon monoxide to carbon dioxide



The carbon dioxide is soluble in cold water, particularly so if passed into it under pressure. Hydrogen is not very soluble, and hence may be obtained easily by this method in a fairly pure state.

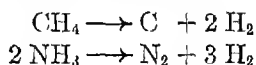
A mixture of carbon monoxide and hydrogen is produced, also, by the reaction of steam with methane and other hydrocarbons — compounds of carbon and hydrogen:



The carbon monoxide is separated from hydrogen by the same procedure as for "water gas."

13. Decomposition of Hydrocarbons and Ammonia

Hydrogen may be produced by decomposing or "cracking" hydrocarbons, such as methane (CH_4), from natural gas, at a sufficiently high temperature. Ammonia is also "cracked" by being heated at 600° in the presence of a catalyst

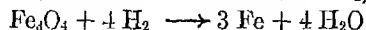
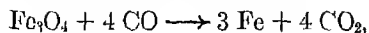


One fourth of the volume of gas produced by the decomposition of ammonia is nitrogen, which cannot be separated easily from hydrogen, but because it is an inactive element, it does not interfere in many of the uses of hydrogen. Because ammonia can be liquefied easily, sufficient quantities of it to produce a large volume of hydrogen (three thousand to four thousand cubic feet) can be shipped in a small cylinder.

14. Steam and Iron

Because of the cheapness of the materials used and the relative purity of the hydrogen produced, this method is very frequently used to produce hydrogen for industrial pur-

poses. This reaction is also used in connection with "water gas." Steam is passed over iron and liberates hydrogen, until the reaction ceases because of the formation of Fe_3O_4 , which coats over and protects the iron from further action. A stream of "water gas" is then passed over the mass, and the following reactions occur:



The iron that has been converted into the oxide is changed back into metallic iron by these reactions, and can be used to liberate more hydrogen from steam. In this manner, the same mass of iron can be used over and over again. In order to make the production of hydrogen continuous, three plant units are sometimes operated. While one unit produces hydrogen, the others reduce the iron oxide to metallic iron.

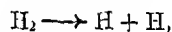
PROPERTIES OF HYDROGEN

15. Physical Properties

Hydrogen is the lightest of the elements, and its density is the smallest of all substances. One liter, measured under standard conditions, weighs 0.08987 g. Because of its small density as compared with air (air is 14.385 times as heavy), hydrogen can be poured upward from one vessel into another. It has no color, taste, or odor, the odor that is noticeable in some samples produced in the laboratory — by the reaction of iron and acids, for example — is caused by small quantities of impurities, some of which are poisonous. Hydrogen can be liquefied at temperatures below -240°C , its critical temperature, by the application of the required pressure. The liquid, which has the appearance of water, has been frozen at temperatures near -260° . This low temperature is obtained by allowing liquid hydrogen to evaporate under reduced pressure. Some heat is required for the evaporation, and this results in a lowering of the temperature of the liquid. The solid has the

appearance of ordinary ice. The solubility of hydrogen in water is slightly less than the solubility of oxygen under the same conditions. At standard pressure and at room temperature, approximately 2 ml of hydrogen dissolves in 100 ml of water.

Hydrogen is *adsorbed* readily by certain metals, and the effect is increased considerably if the metals are in a finely divided, or powdered, condition. Molecules or atoms of adsorbed gases are held *on the surface* of particles of the metals, or perhaps, in some instances, atoms of the metal and hydrogen may chemically combine. This is a different effect than, for example, the *absorption* of water by a sponge. The adsorption of a gas by a solid is sometimes called *occlusion*. As much as 900 ml of hydrogen can be adsorbed by 1 ml of finely divided palladium. This adsorbed hydrogen is very active chemically as indicated by its rapid oxidation in the air, whereas ordinary hydrogen and pure oxygen may be mixed without noticeable reaction unless the mixture is ignited. The increased activity of adsorbed hydrogen indicates that it exists in the atomic (H) instead of the molecular form. Naturally, the atomic form is the more active, since the molecules must first be separated into individual atoms,



before the atoms can react separately with the atoms of other elements.

Because of its extremely small density, hydrogen diffuses more rapidly than any other gas. This property causes considerable loss when hydrogen is used in filling balloons, unless the fabric is coated with some material to prevent the escape of the gas. The diffusion of hydrogen may be demonstrated by passing it into a vessel (Figure 58) which is inverted over a porous cup. The tube, of course, contains air which diffuses outward less rapidly than hydrogen diffuses into the cup. This condition results in an increase of pressure, which causes the water in the bottle to rise in the tube. The frequency of vibration of organ pipes and of the reeds in wind instruments, as well as that of the vocal cords of the larynx, varies inversely with the density of the gas sur-

rounding them. This results in an increased pitch in such instruments when they are made to vibrate in the presence of hydrogen. In the case of the human voice, the pitch is raised when the gas is inhaled.

16. Chemical Properties

At ordinary temperatures, hydrogen does not display pronounced activity in uniting with any of the other elements. Its chemical properties may be summarized as follows:

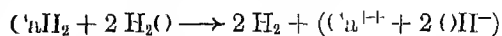
(1) Hydrogen combines with many more non-metals than metals. These combinations are usually very slow at ordinary temperatures, but in many cases they become very rapid at relatively high temperatures. Hydrogen combines with sulfur vapor at 250°C , to form hydrogen sulfide, H_2S . With chlorine the reaction is negligible at low temperatures, but a jet of hydrogen continues to burn in a vessel filled with chlorine. A mixture of the two is easily exploded by exposure to a very bright light; and thus hydrogen chloride (HCl) is formed. Nitrogen and hydrogen combine under proper conditions of temperature and pressure to form ammonia, NH_3 , this reaction is the basis of the Haber process for the production of ammonia. The reaction between oxygen and hydrogen is negligible at temperatures as high as 400°C . At 525°C , considerable water is formed after the mixture has stood several hours. At 600°C , the speed of the reaction is rapid, and at 700° it occurs explosively.

Because of the explosion that is certain to occur if a confined mixture of hydrogen and oxygen (or air) is ignited, great care must be taken in preparing hydrogen. No generator of hydrogen should be set up in the vicinity of a flame, and the hydrogen escaping from a generator should not be lighted until tests show that it is pure. A sample should be collected in a test tube, removed to a distance of several feet from the source, and ignited. If the hydrogen burns quietly it is pure. The safest procedure to follow consists in lighting the hydrogen from the gen-

erator only with a tube of burning hydrogen that has been collected from the same source.

Catalysts, such as finely divided platinum or palladium, accelerate the speed of the reaction even at low temperatures. Owing to the liberation of heat, the catalyst becomes red hot, and heats the hydrogen-oxygen mixture around it to a temperature at which ignition results. The same principle is used in gas-lighters. Many of the combinations of hydrogen with other non-metals are greatly accelerated by catalytic agents. This is particularly true of the production of ammonia by the Haber process.

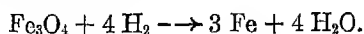
(2) With certain metals, hydrogen forms compounds called *hydrides*. This name is not necessarily restricted to compounds of hydrogen and the metals. We may, for example, refer to hydrogen sulfide, H_2S , as a hydride of sulfur. In compounds of hydrogen with the non-metals, however, the usual practice is to add the suffix *ide* to the name of the non-metal rather than to speak of a hydride. The active metals combine directly with hydrogen when they are heated in its presence. Some metallic hydrides are unstable, a fact that may account for the catalytic action of some metals in reactions involving hydrogen. Hydrogen may be taken up by the metal catalyst to form an unstable hydride which, in turn, liberates hydrogen (perhaps in the atomic state) for reaction with other substances. The tendency to form hydrides may also be partly responsible for the adsorption of hydrogen by certain metals. Examples of metallic hydrides are NaH and CaH_2 . They react with water to liberate hydrogen and to form hydroxides of the metals.



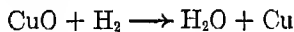
(3) Hydrogen reacts with certain kinds of compounds that already contain some hydrogen. Because of their ability to combine with more hydrogen, these compounds are said to be *unsaturated*, they are organic compounds of carbon and hydrogen, and some of them also contain oxygen and even

other elements. The reaction by which hydrogen is added is called *hydrogenation*. Hydrogen reacts, for example, with unsaturated, liquid fats to form saturated, solid fats. Solid fats made by hydrogenating liquid fats are used as substitutes for butter, for cooking in place of lard, and for making hard soaps.

(4) Hydrogen is a *reducing agent*. As an example of this property, we may recall the following reaction:



Here hydrogen *reduces* iron from its combination with oxygen to metallic iron. Hydrogen reduces the oxides of many other metals in a similar manner:



In each of these reactions hydrogen is said to have been oxidized because its valence number is increased from 0 to +1. In contrast to these cases in which hydrogen acts as a reducing agent, let us recall reactions such as

- (1) $\text{Zn} + 2 (\text{H}^+ + \text{Cl}^-) \rightarrow (\text{Zn}^{++} + 2 \text{Cl}^-) + \text{H}_2$
- (2) $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
- (3) $2 \text{Na} + 2 \text{H}_2\text{O} \rightarrow 2 (\text{Na}^+ + \text{OH}^-) + \text{H}_2$

In each of these reactions hydrogen is *reduced*, while zinc, carbon, and sodium are *oxidized*. (At this time, the student should review the subject of oxidation and reduction as presented on pages 75-77.)

17. Atomic Hydrogen

Hydrogen in the free state is composed of molecules of H_2 . The fact that atoms do not occur singly indicates that the molecule is extremely stable, and that a relatively large quantity of energy is required to dissociate it—to divide it into the single atoms. This dissociation, however, can be accomplished under special conditions, and single atoms do sometimes exist for a brief period of time. For example, the hydrogen that is liberated in the reaction between an acid and a metal is probably set free as single

atoms, which then combine in pairs to form molecules. At the moment of liberation, this hydrogen is very active in reacting with other substances; previously, it was called *nascent* hydrogen—hydrogen in the state “of being born.” The hydrogen that dissolves in melted iron and remains in solution when the iron solidifies, or freezes, is also probably in the atomic state. The extreme activity of the hydrogen adsorbed by finely divided metals is probably the result of the dissociation of hydrogen molecules; single atoms are adsorbed.

Atomic hydrogen forms the same kinds of compounds and takes part in the same kinds of reactions as molecular hydrogen. In these reactions, however, atoms rather than molecules react with atoms of other elements, and we should expect, therefore, that atomic hydrogen would be more active than ordinary hydrogen, because the atoms are already separated and ready to combine with other atoms, while the molecules must be broken up into atoms during the reaction. In keeping with this prediction, we find that reactions which are very slow, at ordinary temperatures, when molecular hydrogen is used without a catalyst, are very rapid when hydrogen is in the atomic form. Atomic hydrogen, for example, is frequently produced in a mixture containing some substance with which it is to react by adding hydrochloric acid and finely divided zinc or some other active metal.

The so-called *atomic hydrogen flame* is produced by passing hydrogen through an electric arc before it burns in an atmosphere of oxygen or air. In the arc, hydrogen is partially dissociated into the atomic form. The recombination of the atoms plus the oxidation of hydrogen to form water liberates a large amount of energy. A temperature of $3500^\circ - 4000^\circ \text{C}$ can be obtained in this flame.

18. Heavy Hydrogen or Deuterium

There are three isotopes (page 51) of hydrogen; these differ in the structures of their atoms and in atomic weights. The ordinary hydrogen atom has a single proton for its nucleus and one electron. Not many years ago, a second kind of hydrogen atom was predicted. It was said that this atom should also have a single electron but that its nucleus should contain one neutron as well as

a proton. Since each kind of atom was thought to have a single electron, it was believed that the two kinds of hydrogen should resemble each other very closely in properties, but that one should have an atomic weight twice that of the other. The heavier kind of hydrogen was called, simply, *heavy hydrogen*.

By studying the spectrum of luminous hydrogen (analyzing the light that it emits), Urey in 1931 showed that both kinds of hydrogen do exist. He studied the gas that was last to evaporate from liquefied hydrogen; the heavier and, therefore, more slowly moving molecules were the last to evaporate. The heavier isotope of hydrogen is now called *deuterium*. It is produced by collecting the final portion of hydrogen liberated in the electrolysis of water, since the lighter atoms are liberated more readily than those of deuterium. For the complete separation of deuterium, the sample first collected is burned to form water, which is again electrolyzed, and the last portion of hydrogen set free is again collected. The procedure may be repeated until pure deuterium is obtained. Pure heavy water, or *deuterium oxide*, is now available for research. Its properties are considerably different from those of ordinary water. It has a different physiological effect on animals that drink it, as compared with an equal volume of water, it dissolves different quantities of salt and other substances, and its density, boiling point, and freezing point differ from those of water. During recent years, great interest has been shown in the preparation of compounds in which hydrogen is replaced by deuterium. Ordinary water contains one molecule of deuterium oxide in about 4500. The most abundant isotope of hydrogen, which has an atomic weight of approximately 1, is sometimes called *protium*.

The atom of the third isotope (*tritium*) contains one electron and its nucleus is composed of one proton and two neutrons. Ordinary hydrogen contains one part of this isotope in several millions.

19. Uses of Hydrogen

(1) The oxygen-hydrogen torch, or *blow-pipe*, has been described on page 73.

(2) As a *reducing agent*, hydrogen is used to reduce the oxides of certain metals by combining with the oxygen they contain and setting the metals free. The tungsten used as the filament in electric-light bulbs is prepared in this manner. Hydrogen is also used to produce a reducing atmosphere about metals that must be heat-treated, as in the annealing of brass. It is also used to produce a non-oxidizing atmosphere about metals that are heated to a high temperature for other reasons, as, for example, the wire used as resistance in certain types of electric furnaces. In all of these instances, the metals would combine with oxygen, if it were not excluded. If any oxidation does occur, hydrogen reduces the oxides that are formed and sets the metals free again.

(3) Hydrogen is used to *fill balloons and dirigibles*. Because of the danger involved in its use, hydrogen is replaced by helium for such purposes, whenever a supply of the latter is available. Helium, unlike hydrogen, is inert, so that its use involves no danger of chance ignition.

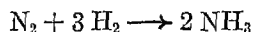
The lifting power of hydrogen in air is greater than that of any other gas, since the buoyant effect of a gas (in air) depends upon the difference between its weight and the weight of the volume of air that it displaces. A gas such as carbon dioxide, CO_2 , would have no lifting power at ordinary temperatures, since it is heavier than air. The densities of hydrogen, helium, and air (standard conditions) are 0.08987, 0.187, and 1.293 grams per liter, respectively. To avoid these small numbers, we may use a larger volume, weighing 2, 4, and 29 grams (weight of 22.4 standard liters), respectively. The buoyant effects of hydrogen and helium are, therefore, in the ratio of (29-2) to (29-4) or 27 to 25. The rates of diffusion of hydrogen and helium are inversely proportional to the square roots of their densities. Thus, hydrogen diffuses $\sqrt{4}/\sqrt{2} = 2/1.415 = 1.4$ times as rapidly as helium. This is not sufficient difference to make helium much more desirable for use in balloons, although its

slower rate of diffusion does decrease somewhat the loss caused by the escape of the gas through the fabric of which the container is made

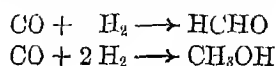
(4) Hydrogen is used to *harden liquid fats* such as coconut and cottonseed oils. Hydrogen under pressure is forced into the liquid fats at temperatures around 175°C , and in the presence of finely divided metal (usually nickel), which acts as a catalyst. The reaction that occurs involves the combination of hydrogen with certain atoms of carbon in the molecules of the liquid fats, which, because of their ability to combine further with hydrogen or other substances, are said to be unsaturated (see page 113). Upon cooling, solid "saturated" fats are obtained. These solid fats are used as substitutes for lard and in the production of candles and hard soaps.

(5) Hydrogen is used in the *synthetic production* of ammonia, NH_3 , methyl alcohol, CH_3OH ; formaldehyde, HCHO , and other substances.

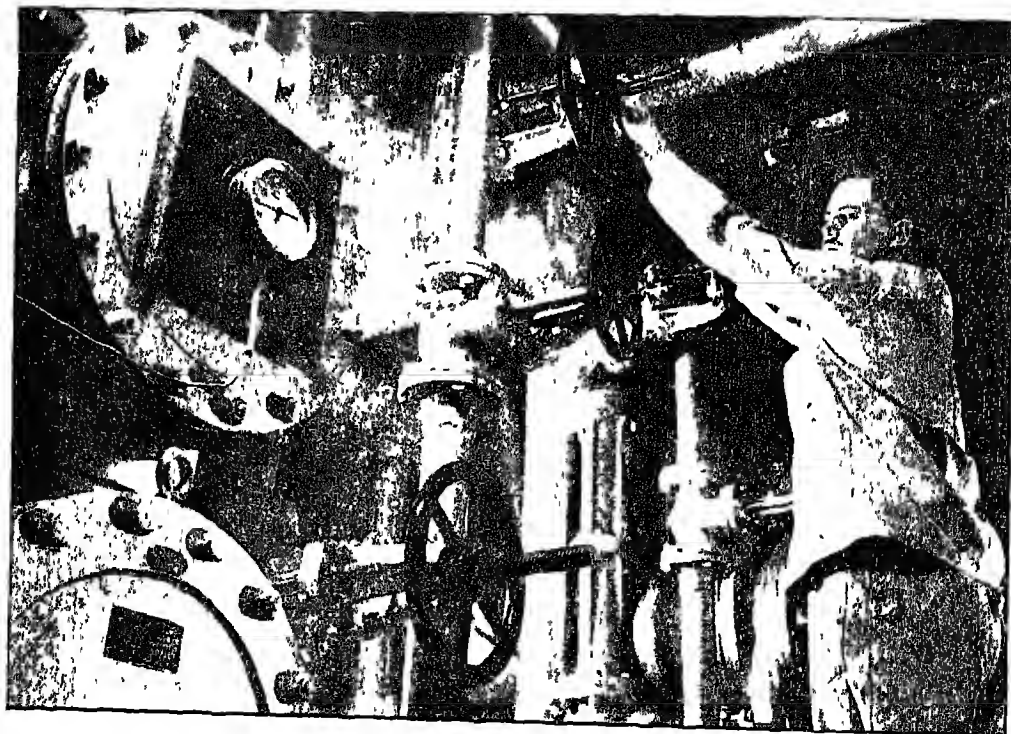
Until about thirty years ago, coal was virtually the only source of ammonia. Some is still obtained from coal, but the synthesis of ammonia from hydrogen and the nitrogen of the air is now a far more important source of supply.



Methyl, or wood alcohol was formerly produced from wood. Its synthesis from carbon monoxide and hydrogen is now the principal source of this important compound. Formaldehyde is synthesized by a similar reaction.



Because of the industrial importance of formaldehyde in the manufacture of certain kinds of plastics, of wood alcohol as a solvent and as a starting material in the synthesis of many dyes, drugs, and other organic compounds, and of ammonia in the manufacture



Courtesy of Lever Brothers

Figure 65. A Section of a Plant in Which Liquid Fats Are Converted Into Solid Fats by Hydrogenation

of fertilizers, nitric acid, and explosives, the rôle of hydrogen in their synthetic production is the most important of the many uses of this element. Certain other compounds containing hydrogen can be synthesized in a similar manner. In some instances the effect upon national and even world-wide economics and industry has been almost revolutionary. At one time, for example, every nation depended upon sodium nitrate, obtainable only from Chile, for the manufacture of nitric acid, which is essential in the production of explosives, fertilizers, and many other products of importance. Now nitric acid can be manufactured in any country from the ammonia that is made from hydrogen and the nitrogen of the air.

20. The Production of Motor Fuels and Oils from Coal

Coal is composed of carbon and compounds of carbon, hydrogen, nitrogen, and a few other elements. Gasoline, kerosene, and lubricating oils are composed of several liquid compounds of carbon and hydrogen; gasoline, for example, contains heptane, C_7H_{16} , and lubricating oils contain similar, but more complex and higher boiling compounds, such as $C_{20}H_{42}$.

If hydrogen could be made to combine with the carbon in coal, liquid hydrocarbons, such as those contained in gasoline, should be formed. This combination has been made to take place by treating powdered coal with hydrogen at moderately high temperatures and under very great pressures. The process, which has been developed on a large scale in Germany since 1925, is called the Bergius process for the liquefaction of coal. That it is a practical method of producing motor fuels is shown by Germany's production, even as early as 1929, of 100,000 tons of liquid fuels through its operation. Plants for the operation of this process have been built in our own country, also. As a means of producing liquid fuels, this process is of the greatest importance to those countries in which natural resources of petroleum —

from which gasoline, kerosene, lubricating oil, fuel oil, and similar products are obtained by distillation — do not exist or have been exhausted.

By a somewhat similar process, hydrocarbons for use as motor fuel are produced by catalyzed reactions from a mixture of carbon monoxide and hydrogen that results from the reaction of coke and steam (water gas) or from the reaction of steam with methane (CH_4). Hydrogen is also used in the hydrogenation of crude petroleum to increase the quantity of gasoline that can be produced.

Review Exercises

- 1 Compare and contrast oxygen and hydrogen as to physical and chemical properties.
- 2 How could the hydrogen that escapes from the earth in the gases from some volcanoes have been produced from water? Why should such gases be more likely to contain hydrogen than oxygen?
- 3 What two reactions discussed in this chapter involve water as an oxidizing agent? Name one reaction in which hydrogen acts as a reducing agent.
- 4 Name four reactions by which hydrogen can be produced from water.
- 5 Why are laboratory samples of hydrogen not often produced by the electrolysis of water? Why is industrial hydrogen not produced by the reaction between acids and metals?
- 6 Why cannot sodium hydroxide be regarded as a catalyst in the production of hydrogen by means of the reaction involving silicon?
- 7 Name four uses of hydrogen and describe the chemical changes upon which they depend.
- 8 Why does an oxygen-hydrogen blowpipe give a hotter flame than one in which a mixture of hydrogen and air is burned?
- 9 Could a balloon filled with hydrogen rise to an unlimited altitude? Explain.
- 10 Which of the following metals displace tin from a solution containing stannous chloride, $SnCl_2$? Copper, gold, magnesium, iron, lead, aluminum, platinum, and silver. Which of these metals would tin displace?
- 11 How could you prove that one of the elements

- of which a sheet of paper is composed is hydrogen?
- 12 Why would the name oxygen have been more appropriate for the element now called hydrogen than it is for the element to which it is applied?
 - 13 Explain oxidation and reduction in terms of changes involving the electrons of atoms
 - 14 Why does hydrogen combine more readily with non-metals than with metals?
 - 15 Under what condition will a reversible reaction occur only in one direction?
 - 16 Explain the displacement of one metal from its compounds by another metal, or by hydrogen, in terms of changes involving electrons
 - 17 When iron displaces copper from cupric chloride, CuCl_2 , which element is the oxidizing agent and which is the reducing agent?
 - 18 Why was the production of gasoline by the hydrogenation of coal more widely used in Germany than in the United States even prior to 1939?
 - 19 Calculate the (standard) volume of 10 kilograms of hydrogen
 - 20 A balloon contains 100 kg of hydrogen and weighs one ton. Will the balloon rise if the hydrogen is under standard conditions?
 - 21 A balloon is filled with hydrogen at a pressure of 740 mm and at 30°C . It contains 3000 cubic feet. What will the volume become when the balloon has risen to an altitude where the temperature is 10°C . and the pressure is 60 mm?

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MOLECULES AND MOLECULAR WEIGHTS

It seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable, movable parturles, of such sizes and figures, and with such other properties, and in such proportion to space as most conduced to the end for which he formed them, and that these primitive particles, being solids, are incomparably harder than any porous body compounded of them, even so very hard as never to wear or break in pieces, no ordinary power being able to divide what God himself made one in the first creation

SIR ISAAC NEWTON

1 Introduction

The reader who has followed the discussion of the eight preceding chapters has been introduced to many arguments in favor of the view that matter is composed of particles. The laws of chemical change and the kinetic interpretation of the behavior of gases make any other conclusion almost impossible. Our presentation of the atomic-molecular theory, however, is far from complete, and in some respects we have developed it only a little further than it was carried by John Dalton in the early years of the nineteenth century. By 1860, many uncertainties under which Dalton labored had been fairly well cleared away, and certain fundamental principles were generally accepted. Among these was recognition of the distinction between atoms and molecules of certain elements, the true basis upon which the formulas of compounds and the number of atoms of each kind in a molecule could be determined, and accurate methods of determining the relative weights of atoms and molecules. To these subjects we now turn our attention. First of all, we shall study the relations between the volumes of gases that react or are produced

during chemical changes, because in such studies were found the clues upon which the nineteenth-century development of chemistry was based.

2. Reactions Involving Gases

Whenever water is produced from its elements, two volumes of hydrogen are required for one volume of oxygen. If the water produced by the reaction is kept at 100° C, or higher, it too will exist as a gas (water vapor), and its volume, calculated for the same pressure and temperature as the volumes of hydrogen and oxygen, will be the same as that of hydrogen and twice that of oxygen — two volumes. We use the term *volume* here in a general sense. If the volume of one gas is measured in liters, the volumes of the others must also be measured in liters. Thus, two liters of hydrogen and one liter of oxygen react to form two liters of water vapor, all volumes being calculated for the same temperature and pressure.

Below, we list several other reactions that involve gases. These statements point out the relative volumes of the gases that react or are produced in each reaction, and it is

upon this point that our attention at present should be centered

- (1) Carbon (solid, as in charcoal) + 1 volume of oxygen \longrightarrow 1 volume of carbon dioxide
- (2) 1 volume of hydrogen + 1 volume of chlorine \longrightarrow 2 volumes of hydrogen chloride
- (3) 1 volume of nitrogen + 3 volumes of hydrogen \longrightarrow 2 volumes of ammonia
- (4) mercuric oxide (solid) \longrightarrow 2 volumes of mercury vapor + 1 volume of oxygen

Since we are concerned *only with gases*, the volumes of the solids involved in the reactions are not considered

3 Gay-Lussac's Law of Combining Volumes of Gases

From a study of such reactions as those described above, Gay Lussac, in 1808, formulated the general principle that bears his name *The volumes of any two gases involved in a reaction, either as reacting substances or as products of the reaction, are in a ratio to each other of two small, whole numbers*. Thus, the volumes of hydrogen and oxygen in the reaction to form water are in the ratio of two to one, the ratio of the volumes of hydrogen and water vapor is one to one, and that of oxygen and water vapor is one to two.

This law had more influence upon the development of chemistry than even the Law of Combining Proportions by Weight. For one thing, it is much simpler and more easily explained. The study of the combining *weights* of the elements involves fairly large numbers, each of which concerns only one substance, and most of which — as 35.46 for chlorine — are not whole numbers. On the other hand, a few small numbers — 1, 2, 3, 4, but usually nothing higher — can be used to represent the proportions by volume of all gases, both elements and compounds, in their reactions.

We come now to this question. Why are the volumes of two gases that take part in, or are produced by a reaction, always in the ratio of two small, whole numbers? The answer has great significance.

4. An Explanation of the Law of Combining Volumes

Let us try to formulate a theory concerning the structure and composition of gases that will answer this question in a satisfactory manner. The clues for the solution of the problem are to be found in facts previously studied and in certain conclusions that we have already reached as to the nature of matter.

(1) In arriving at the kinetic theory, we have accepted the conclusion that gases are composed of particles separated by empty space.

(2) Dalton's atomic theory leads us to believe that when two elements react — just now we are interested in two gaseous elements, such as hydrogen and oxygen — their two kinds of *particles* react in simple, numerical ratios, such as two to one, to make one or more whole particles of a compound.

(3) Gay-Lussac's law states that the volumes of any two gases that react, or are produced, in a reaction are also in a ratio of two small, whole numbers.

5. The Reaction of Hydrogen and Oxygen

Accepting, then, these three statements, we see that the particles of gases that react, or are produced, are in the ratio to each other of small, whole numbers, so, too, are the volumes of the gases. The indication is that the *numbers of particles* that react are in the same ratio as the *volumes*. For example, the volumes of hydrogen and oxygen that combine to form water are in the ratio of two to one, perhaps the particles of hydrogen and oxygen that combine are also in the ratio of two to one.

At any rate, let us build our explanation around this assumption. If it is true, then *equal volumes of hydrogen, oxygen, and all other gases contain the same number of particles* under the same conditions of temperature and pressure. Two volumes of hydrogen combine with one volume of oxygen, then, if two particles of hydrogen combine with one particle of oxygen, it is clear that equal volumes of hydrogen and oxygen contain the same number of particles.

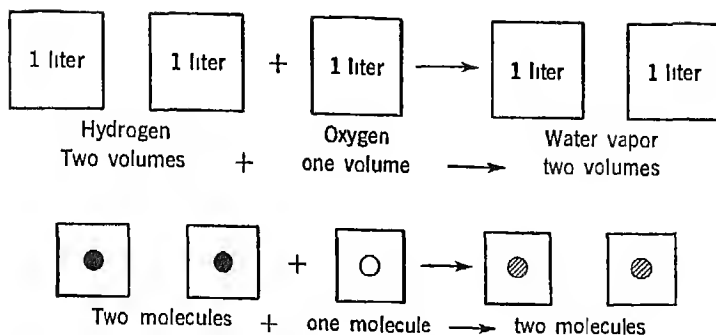
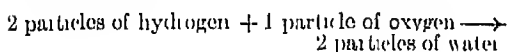


Figure 66 The Reaction of Hydrogen and Oxygen

If equal volumes of different gases contain the same number of molecules, it is obvious that the molecules that react and are produced are in the same proportion as the volumes of the different gases involved in the reaction

Next, we note that two volumes of water vapor are formed when two volumes of hydrogen and one of oxygen react. Still relying upon our conclusion that equal volumes of all gases contain the same number of particles (assuming constant temperature and pressure), the number of particles of water must be the same as the number of hydrogen particles and twice as great as the number of oxygen particles from which water is made. See Figure 66.



6. The Reaction of Hydrogen and Chlorine

In this reaction (Figure 67), one volume of hydrogen reacts with an equal volume of chlorine to form two volumes of hydrogen chloride, which is also a gas. (The temperature and pressure for which these volumes are calculated are, of course, the same for all three gases.) If equal volumes of these gases contain the same number of particles, then one particle of hydrogen reacts with one of chlorine to make two of hydrogen chloride.

Why should two liters of hydrogen react with one of oxygen, while only one liter of hydrogen is required to react with one of

chlorine? Surely, the answer must be that twice as many particles of hydrogen react with one particle of oxygen as react with one of chlorine. Our assumption that equal volumes of gases contain the same number of particles appears to hold up very well.

7 The Reaction of Hydrogen and Nitrogen

In this reaction, one volume of nitrogen and three volumes of hydrogen form two volumes of ammonia. Using the same line of reasoning as before, we conclude that three particles of hydrogen and one of nitrogen form two of ammonia (Figure 68).

8 Avogadro's Principle

The explanation of Gay-Lussac's law that we have used above was first suggested by Avogadro in 1811. The fundamental idea upon which this explanation was based is called Avogadro's Principle: *Equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules.* The word *molecule* was first used in this connection. Avogadro used it to designate the smallest particle of a substance that exists in the natural state of that substance — the smallest particle that can exist

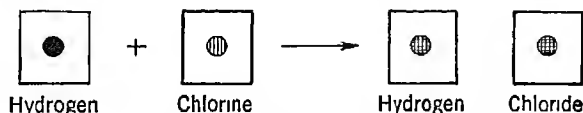


Figure 67 The Reaction of Hydrogen and Chlorine

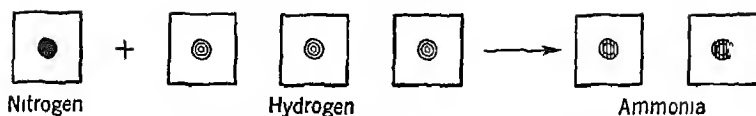


Figure 68. The Reaction of Hydrogen and Nitrogen

alone. Thus, the particles of hydrogen, oxygen, chlorine, nitrogen, water, hydrogen chloride, and ammonia to which we have referred in the preceding sections are molecules — not atoms — of these substances. Although Avogadro's principle was based upon an assumption, and therefore was at first only a hypothesis, it has been verified so completely by experimental data that it can now be called a law.

ATOMS AND MOLECULES

Avogadro's principle was introduced in the early part of the nineteenth century, but not until after the middle of the century was it accepted generally, and its full worth realized. Its final recognition and its permanent establishment in the basic framework of chemistry must be credited to Cannizzaro, who revived the law and showed that it is the only logical basis for distinguishing between the atoms and molecules of elements and for the accurate determination of the relative weights of atoms and molecules of different substances. The story of how Cannizzaro unraveled these tangled threads of early nineteenth-century chemistry, reconciled different views, and placed chemistry at last upon a sound foundation, is told in the pages that follow.

9 Atoms and Molecules of Elements: How Many Atoms in a Molecule of Hydrogen?

Following along the line of reasoning that led to Avogadro's principle, it appears that one particle — the smallest possible particle that can exist by itself — of hydrogen reacts with one of chlorine to make two of hydrogen chloride. We shall call these particles molecules. Each molecule of hydrogen chloride must contain some hydrogen, and all samples

of hydrogen chloride are identical in properties and in composition, hence the different molecules of hydrogen chloride must contain the *same quantity* of hydrogen. This must mean that the molecule of hydrogen is composed of at least two identical parts, each of which forms one molecule of hydrogen chloride. For the same reason the chlorine molecule must also contain at least two parts. The whole particles of hydrogen and chlorine, and also the particles of hydrogen chloride, are molecules of these substances.

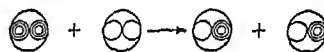
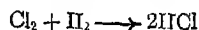


Figure 69.



The parts, or fractions, of the molecules of hydrogen and chlorine must be considered as atoms of these elements, in keeping with the definition of an atom as *the smallest portion of an element that takes part in a chemical reaction*.

The atom of an element, therefore, is not necessarily the smallest particle of an element that occurs in the free state, such a particle is a molecule. The smallest particles of hydrogen and chlorine in the original volumes of these gases — before they react — are molecules. After the reaction, the smallest portions of these elements in molecules of hydrogen chloride are atoms. It appears, therefore, that each molecule of hydrogen, and also each one of chlorine, contains at least two atoms. If molecules of hydrogen chloride are decomposed, single atoms of hydrogen and of chlorine are liberated, but immediately the atoms of each element combine to make molecules because the single atoms cannot exist in the free state of these elements.

10. Is It Possible That a Molecule of Hydrogen Contains More than Two Atoms?

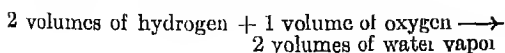
If hydrogen and chlorine molecules are composed of two atoms each, then each molecule of hydrogen chloride contains one atom each of hydrogen and chlorine, and the formula of the compound is HCl (See Figure 69). There are, of course, other possibilities. Each molecule of hydrogen and each molecule of chlorine might contain four (or six or eight) atoms, each molecule of hydrogen chloride would then contain two (or three or four) atoms of each of the elements.

This question can be answered satisfactorily only when we know the relative weights of hydrogen chloride molecules and hydrogen and chlorine atoms. If the weight of the molecule of hydrogen chloride is equal to the sum of the weights of one atom each of hydrogen and chlorine, then there can be no doubt that the molecule (HCl) is composed of one atom of each of the two elements. If the molecular weight, however, is double the weight of the simplest possible molecule, then the molecule (H_2Cl_2) must contain two atoms each of hydrogen and chlorine, and so on. Naturally, no decision can be made in this matter until the basis for the determination of atomic and molecular weights is fully worked out and agreed upon.

We shall describe the methods used to determine the relative weights of different atoms and molecules a little later. One reason for doing so is indicated by the question we have just raised. We shall find that all evidence points toward HCl as the correct formula for hydrogen chloride, and therefore to the conclusion that a molecule of this substance contains only two atoms, one of each element.

11. The Reaction of Hydrogen and Oxygen

The reaction between oxygen and hydrogen to form water indicates that the oxygen molecule is composed of two atoms.



Hence, in accordance with Avogadro's law, we conclude that

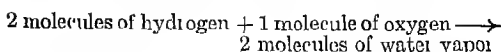
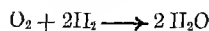


Figure 70



We must assume that one half of the oxygen molecule goes into each of the water molecules and that the molecule of oxygen is probably diatomic — O_2 . As in the case of hydrogen and chlorine above, the oxygen molecule, so far as our evidence to this point proves anything, might contain some multiple of two atoms (4, 6, 8, etc.). However, the molecular weight of water as determined by the method to be described in Section 13, is 18.016, which shows that the water molecule can contain but one atom of oxygen. The molecule of oxygen, therefore, is O_2 .

Since each hydrogen molecule also contains two atoms, as indicated by the reaction between hydrogen and chlorine, we may say that four atoms of hydrogen, which exist in the free state in the form of two diatomic molecules, react with two atoms of oxygen, which exist in the free state as a single diatomic molecule. Two molecules of water are produced by this reaction, and each of these is composed of two atoms of hydrogen and one atom of oxygen. The formula of water, therefore, is H_2O .

12. Molecules of Other Elements

The molecules of some elements, such as the inert gases of the atmosphere, are monatomic, i.e., their molecules consist of single atoms. For these elements, therefore, the terms molecule and atom refer to the same particle of the element. Many other gaseous elements, including nitrogen, oxygen, chlorine, and hydrogen, are diatomic, i.e., their molecules consist of two atoms each. In the absence of definite information concerning their molecular composition, many solid elements are regarded as monatomic. When

these same elements can be obtained and studied in their gaseous state, definite molecular formulas (the number of atoms in a molecule) can sometimes be determined. Thus, sulfur, at temperatures slightly above its boiling point, appears to consist of molecules of S_8 . At higher temperatures, the molecules contain fewer atoms, most of them having the formula S_2 . The solid state of sulfur is usually regarded as consisting of single atoms, S.

13. A Comparison of the Weights of Molecules

Avogadro's principle provides a means of determining the relative weights of molecules of different substances in the gaseous state. Equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules, hence, if we wish to compare the weights of the molecules of two gases, all that we need to do is to find the weights of equal volumes of the two.

If it were possible to select the volumes of the two gases that contain *single* molecules, the weights of these volumes would give the absolute weights of the two molecules. But we cannot deal with volumes as small as these. If, however, we select a definite weight of some gas as a standard, then its volume and an equal volume of any other gas (at the same temperature and pressure) will contain the *same number* of molecules. Therefore, the two kinds of molecules will have weights that are in the same ratio as the weights of equal volumes of the two gases. We do not need to know the number of molecules weighed, the ratio of the weights of 100,000,000, or of any other number of molecules of two substances, is the same as the ratio of the weights of one molecule of each.

Since it combines with a large number of elements, oxygen has been selected as the standard. Some weight of oxygen must also be selected for the comparisons so that the volume to be used for different gases can be fixed. Let us use 32 g of oxygen, this weight of the element occupies 22.4 liters under standard conditions. Now, by Avogadro's principle, the weight (2.016 g) of 22.4 liters

of hydrogen, under standard conditions, is the weight of a certain number of hydrogen molecules as compared with 32 g as the weight of the same number of oxygen molecules. For our present purposes, it is not necessary that we know what that number is, let us designate it by x . Then x molecules of hydrogen weigh 2.016 g, and x molecules of oxygen weigh 32 g.

$$\frac{\text{weight of } x \text{ molecules of oxygen}}{\text{weight of } x \text{ molecules of hydrogen}} = \frac{\text{weight of 1 molecule of oxygen}}{\text{weight of 1 molecule of hydrogen}} = \frac{32}{2.016}.$$

In other words, whatever a single molecule of oxygen weighs, a molecule of hydrogen weighs 2.016/32 of that weight, the molecular weight of hydrogen is 2.016 as compared with 32 for oxygen. In general,

$$\frac{\text{weight of 22.4 liters of } X}{\text{weight of 22.4 liters of } O_2} = \frac{\text{weight of 1 molecule of } X}{\text{weight of 1 molecule of } O_2} = \frac{a}{32},$$

where a is the weight of a molecule of the substance X , as compared with 32 for the weight of a molecule of oxygen, thus, a grams of X is the weight of 22.4 standard liters of X in its gaseous state.

14. The Scale of Molecular Weights

The scale of molecular weights is based, therefore, upon the selection of the number 32 to represent the weight of a molecule of oxygen. Since a molecule of this element contains two atoms, the selection of this number places molecular and atomic weights on the same scale, namely, a scale on which the weight of an atom of oxygen is represented by 16.

The molecular weights of other substances, expressed on the same scale, are nitrogen 28, carbon dioxide 44, water 18.016, chlorine 70.92, sulfur dioxide 64, ammonia 17.024, hydrogen chloride 36.468. These numbers mean that 32 parts (grams, pounds, tons, and the like) of oxygen contain the same number of molecules as 28 parts of nitrogen,

44 parts of carbon dioxide, and so on. They also mean that the weights of equal numbers of molecules of oxygen and nitrogen are in the ratio of 32 to 28, the number of molecules can be one of each substance, or any other number provided it is the same for both.

15. Gram-Molecular Weights and Gram-Molecular Volumes

In research and in the everyday work of the chemist, it is often necessary to use the same number of molecules of different substances, at least, we must be able to calculate the *relative* numbers of molecules of different substances when the weights to be used are known. Whenever these weights are in the same ratio as the molecular weights, we are certain that we are dealing with the same number of molecules of each substance. If, for example, 11 g of carbon dioxide (molecular weight, 44) and 32 g of sulfur dioxide (molecular weight, 64) are involved in a reaction, we know that two molecules of the latter are involved for each molecule of the former.

$$\begin{aligned}\frac{11 \text{ g}}{44 \text{ g}} &= 0.25 \text{ gram-molecular weight of} \\ &\quad \text{carbon dioxide} \\ \frac{32 \text{ g}}{64 \text{ g}} &= 0.50 \text{ gram-molecular weight of} \\ &\quad \text{sulfur dioxide}\end{aligned}$$

There are twice as many molecules in 0.5 of a gram-molecular weight as in 0.25.

The *gram-molecular weight* of any substance is the number of grams of that substance that corresponds to the molecular weight. 32 g of oxygen, 2.016 g of hydrogen, and 28 g of nitrogen. Under standard conditions, the gram-molecular weight of oxygen (32 g) occupies 22.4 liters. A gram-molecular weight of any other gas, under the same conditions, occupies the same volume, which is called, therefore, the *gram-molecular volume*.

16. Mole and Mole-Volume

The term *molar weight* and *mole* are often used in place of gram-molecular weight.

Thus, in speaking of 32 g of oxygen we may use the expression *one mole* of oxygen instead of *one gram-molecular weight*. Similarly, we speak of the volume occupied by one mole of a substance in its gaseous state as the *gram-molecular, molar, or mole-volume*.

17. Calculation of the Gram-Molecular Weight from Laboratory Data

In finding the molecular weight of a gas it is not necessary to weigh 22.4 liters of the gas. Neither is it necessary for the volume that is weighed to be measured at 0° and under a pressure of 760 mm. We may find, for example, that the volume of a definite quantity of a gas, at 20° C. and under a pressure of 720 mm, is 200 ml, and that the weight of this volume is 1.0 g. To determine the weight of 22.4 liters of the same gas under standard conditions, the volume as measured at the observed temperature and pressure must be corrected for the change to standard conditions. If the gas is collected over water, an additional correction must be made in the usual manner for the vapor pressure of water. For the sample of gas described above, the volume is 200 ml, the temperature is 20° C, and the pressure is 720 mm. The volume of the same sample under standard conditions can be calculated as follows:

$$\begin{aligned}\text{Volume (standard)} &= \\ 200 \times 273 / 293 \times 720 / 760 &= 176.54 \text{ ml}\end{aligned}$$

(If the gas is collected over water, the aqueous vapor pressure of 17.5 mm must be subtracted from 720 mm before making the above calculations.)

The weight of 176.54 ml of the gas under standard conditions is 1.0 g, since the weight is the same at all temperatures and under all pressures, provided that none of the substance is removed and no more added. The number of molecules also remains the same under all conditions, unless molecules are added or removed. Now that the weight of 176.54 ml of the gas is known, the calculation of the weight of 22.4 liters is a very simple matter: the weight of 22.4 liters will be as many times 1.0 g as 22.4 liters is times 176.54 ml.

$$\begin{aligned}22.4 \text{ liters} &= 22,400 \text{ ml} \\ 22,400 / 176.54 \times 1.0 &= 126.8 \text{ g}\end{aligned}$$

The weight of 22.4 liters of the gas under standard conditions is 126.8 g. This is the gram-molecular weight of the gas, and the number 126.8 represents the weight of a molecule as compared to the weight of a molecule of oxygen on a scale in which the latter is represented by the number 32.

18. Molecular Weights of Liquids and Solids

The method described for the determination of the molecular weights of gases cannot be applied to substances in their liquid or solid states. If a solid or a liquid can be vaporized, the weight of a definite volume, measured at any temperature and pressure, can be employed to calculate the weight of 22.4 liters of the vapor under standard conditions. Since the weight does not change when the vapor is converted into the liquid or solid states, or *vice versa*, and since the number of molecules of many substances can be assumed to remain the same during the transition from one state to another, the molecular weight of the substance in the vapor state can frequently be taken also as the molecular weight of the substance in its liquid or solid states. But this is not always true. There are substances that are composed of one type of molecule in the vapor state and of another kind in the liquid or solid state. Furthermore, the complexity of the molecule may vary with the temperature for the same state. Thus, at temperatures slightly above the boiling point of liquid sulfur, sulfur vapor exists as molecules containing eight atoms of sulfur (S_8), while at higher temperatures, molecules of S_2 predominate. Similarly, water vapor, and also the liquid under increased pressure at temperatures above 100°C , appears to be composed of simple molecules (H_2O), consisting of two atoms of hydrogen and one of oxygen. At lower temperatures, the molecules appear to be $(H_2O)_2$ or $(H_2O)_3$. If $(H_2O)_2$ molecules replace H_2O molecules in water, the number of molecules is reduced one half, but the molecular weight is twice as large, since the total weight remains the same.

Many substances cannot be obtained con-

veniently, and some not at all, in the gaseous state. To determine the relative weights of the molecules of these substances, other methods must be employed. If the substance dissolves in water, or in some other solvent, the molecular weight can be determined by studying the effect of a given weight of the substance upon the properties of a fixed weight of the substance in which it dissolves. The properties usually studied for this purpose are the boiling and freezing points of the liquid that acts as the solvent.

The boiling point of the solvent is raised, and the freezing point is lowered by the substance that dissolves, and the effect depends upon the *number of molecules* added to a definite quantity of the solvent. The effect is the same for the same number of molecules of different substances. A gram-molecular weight contains the same number of molecules, whatever the substance may be so long as it is a substance composed of molecules. Hence, when a gram-molecular weight of any substance is added to 1000 g. of a certain solvent, such as water, the freezing point and the boiling point should always be affected to the same extent by different substances.

A method by which molecular weights can be determined by the use of this principle is described below. It can be used only when there is no change, such as a reaction between the dissolved substance and the solvent, that alters the total number of molecules. And it can be used only to determine the molecular weights of substances composed of molecules — not ions. It cannot be applied to the solution of sodium chloride ($Na^+ + Cl^-$) or any other ionic compound. The solution of sodium chloride contains two kinds of particles, Na^+ and Cl^- , and each of these has the same effect upon the properties of the solution as a molecule.

19. Molecular Weights by the Boiling and Freezing Point Methods

For aqueous solutions, one gram-molecular weight of cane sugar, for example, dissolved in 1000 g. of water raises the boiling point of

water to 100.53°C , and lowers the freezing point to -1.86°C . Now, if we wish to determine the molecular weight of some other substance that is also soluble in water, we may proceed upon the basis that the weight of the substance which, when dissolved in 1000 g. of water, also lowers the freezing point of the water -1.86° and elevates the boiling point 0.53° is the molecular weight (in grams)

Let us say that 10 g. of substance X dissolved in 100 g. of water lowers the freezing point of the water from 0° to -0.46°C . Let M represent the gram-molecular weight of X . Then

10 g. of X in 100 g. of water lowers f. p. 0.46° , or
 100 g. of X in 1000 g. of water lowers f. p. 0.46°
 M g. of X in 1000 g. of water lowers f. p. 1.86°
 100 g. of X lowers the freezing point of water
 $0.46/1.86$ as much as M g. of X

Therefore,

$$M = \frac{1.86}{0.46} \times 100 \text{ g.} = 404.4 \text{ g.}$$

This method assumes that there is no chemical reaction between the water and the substance dissolved in it and that the solution is a simple mixture of the independent molecules of the two substances. Since this condition is seldom, if ever, attained in an actual solution, the determination of molecular weights by this method is subject to at least small sources of error. It may be used, however, to decide whether the simplest possible formula of a substance, or some other, is the actual formula. Thus the method shows that the molecular weight of glucose (another sugar) is somewhere near 180 and not 360. This indicates clearly, therefore, that the correct formula of glucose is $\text{C}_6\text{H}_{12}\text{O}_6$ and not $\text{C}_{12}\text{H}_{24}\text{O}_{12}$.

The same method can be used to determine the molecular weight of substances that are not soluble in water, if some other solvent can be used. Thus, the molecular weight of naphthalene (moth-balls) can be determined by finding the effect of a definite weight of this substance upon the freezing point of a definite weight (1000 grams) of benzene. Of course, the lowering produced by a gram-molecular weight of the dissolved substance upon the freezing point of 1000 grams of benzene

must be used, instead of 1.86° for aqueous solutions. This value for benzene is 4.9° .

20 Determination of Molecular Weights from the Formulas of Compounds

If we know the formula of a compound, we can calculate its molecular weight as the sum of the atomic weights of the elements. In finding the sum, each atomic weight must be considered as many times as the atom of the element is represented in the formula. Thus, the formula for sucrose (cane sugar) is $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ and the molecular weight is

$$(12 \times 12) + (22 \times 1.008) + (11 \times 16) = 342.18$$

21. Avogadro's Number

The number of molecules in one gram-molecular weight is the same for all substances composed of molecules, it is called Avogadro's number and can be determined by several indirect methods. Molecules cannot be counted directly, of course, because they are not visible, and even if they were visible, they still could not be counted one by one, because the number in a gram-molecular weight is too great. The value of Avogadro's number now generally accepted is 6.0228×10^{23} or 602,280,000,000,000,000,000. In future references to Avogadro's number we shall use the value of 6.023×10^{23} .

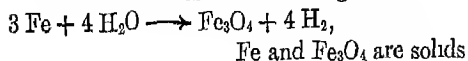
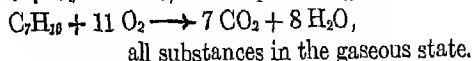
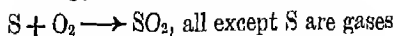
The student may look somewhat suspiciously upon a value so large, especially since it concerns a thing so intangible and so small as a molecule. Later (Chapter 18), we shall describe one of the methods by which this number can be calculated.

<p>Nitrogen 28 grams 1 g. mol wt 6.023×10^{23} molecules 0°C. 760 mm pressure</p>	<p>Oxygen 32 grams 1 g mol wt. 6.023×10^{23} molecules 0°C. 760 mm pressure</p>
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Figure 71. A Comparison of 22.4 Liters Each of Nitrogen and Oxygen

Review Exercises

1. State Gay-Lussac's law of combining volumes and explain the statement by means of appropriate illustrations
2. What are the proportions of the volumes of gases involved in the following reactions? (Recall that the same number of molecules occupy the same volume)



3. What explanation is offered for the reaction of *two* volumes of hydrogen with *one* volume of oxygen to form only *two* volumes of water vapor?
4. What important assumption was originally made in arriving at this explanation?
5. Using this assumption, explain the volume relations in the reaction of (1) hydrogen and chlorine and (2) hydrogen and nitrogen
6. Show how Avogadro's law makes possible a method of determining the molecular weights of gases
7. How is a molecule of hydrogen or chlorine different from an atom of these elements?
8. By what line of reasoning do we conclude that a molecule of hydrogen contains at least two atoms?
9. How can we show that a molecule of oxygen contains two atoms, and that two atoms of hydrogen react with one atom of oxygen to form water?
10. What is the meaning of the term *molecular weight* as applied to an element or a compound? Why is 22.4 liters, rather than some other volume, used in determining the molecular weights of gases?
11. Starting with the weight of any volume of a pure gas at any pressure and temperature, show how you would calculate the molecular weight.
12. How can the molecular weights of some liquids and solids be determined?
13. Define Avogadro's number.
14. A liter (under standard conditions) of each of three gases weighs 0.178, 2.85, and 6.87 grams, respectively. Calculate the molecular weights of the three gases
15. The density of a gas as compared to air (under standard conditions) is 2.45. Calculate the molecular weight of the gas
16. A sample of hydrogen sulfide, H_2S , occupies 643 ml at a certain temperature and pressure and weighs 0.952 g. What is the molecular weight of another gas if 2.105 g of it occupies 1422 ml, at the same temperature and pressure?
17. Calculate the molecular weights of compounds having the following formulas: ethyl alcohol, C_2H_5OH , carbon tetrachloride, CCl_4 , ammonia, NH_3 , toluene, $C_6H_5CH_3$, and glucose, $C_6H_{12}O_6$
18. What would the gram-molecular volume of gaseous substances be if the molecular weight of oxygen were arbitrarily fixed as 50 instead of 32?
19. What is the weight of 22.4 (standard) liters of CS_2 ? Of 10 liters? (Consider the gaseous state of CS_2 .)
20. What (standard) volume would 20 g of carbon disulfide, CS_2 , vapor occupy?

References for Further Reading

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ATOMIC WEIGHTS AND COMBINING CAPACITY

I demand of every chemical principle that it agree with the sum total of chemical theory and be capable of incorporation therewith. Otherwise I must reject it until such time as uncontested evidence in its favor makes it necessary to recast the entire system.

BERZELIUS

1. Introduction

Now that we have learned how molecular weights are determined, we shall turn our attention to atomic weights. First, two approximate methods will be discussed, and later the more exact and more generally used method will be explained. As we study this chapter, we should keep in mind our definition of an atom as the smallest particle of an element that takes part in a chemical change. *This means, then, that the smallest weight of the element found in the molecular weight of any of the compounds of the elements should be the atomic weight.* Since atoms cannot be weighed individually, we must continue to express their relative weights by comparing them with the weight of an atom of oxygen.

We shall also study differences in the *combining capacities* of the atoms of different elements and methods by which they can be determined. This subject has previously been considered (page 58) from the point of view of the structures of atoms. Our concern with the subject in this chapter has to do with chemical methods of determining valence numbers. These methods were in use long before anything at all was known about

the structures of atoms, and they are still of vast importance to the chemist.

DETERMINATIONS OF ATOMIC WEIGHTS

2 Method Based upon the Principle of Dulong and Petit

One of the earliest methods of determining the atomic weights of the elements was suggested by Dulong and Petit in 1818. Their method provided only an approximation of the actual atomic weight and was used primarily to determine which of the different values represented by the combining proportions (by weight) of an element appeared to be the best choice for the atomic weight. The combining proportions of magnesium, for example, show (page 42) that the atomic weight, as compared with 16 for oxygen, should be (approximately) 24 or some multiple or sub-multiple of 24, e.g., 48, 72, 12, 6, and so on. By the procedure now to be described, it can be shown that 24, rather than any of the other numbers mentioned, is the real atomic weight of magnesium.

Dulong and Petit pointed out that the product of the atomic weight of an element *in the solid state* multiplied by the specific

heat of the substance is approximately the same for all elements. This product is usually between 6 and 7, and the average is 6.4

Element	Atomic Weight	Specific Heat	Product Atomic Weight \times Specific Heat
Sodium	23	0.29	6.7
Magnesium	24.3	0.245	6.0
Phosphorus	31	0.20	6.2
Iron	55.8	0.112	6.3
Gold	197.2	0.032	6.3
Mercury (solid)	200.6	0.0335	6.7

The specific heat of a substance is defined as the quantity of heat (in calories) required to raise the temperature of one gram of the substance one degree (C.). A calorie is defined as the quantity of heat required to raise the temperature of 1 g of water 1° C.

$$\text{Atomic weight} \times \text{specific heat} = 6.4$$

$$\text{Atomic weight} = 6.4 / \text{specific heat}$$

If the specific heat of a solid element is known, the approximate atomic weight can be calculated in the manner indicated by the above equation. The value so obtained is not the actual atomic weight. A more accurate value may be obtained by selecting from the different weights that represent the combining proportions of the element (on the basis of 16 parts of oxygen) that weight which is nearest the value calculated from the specific heat. Thus, for copper we find that both 63.6 and 127.2 parts of this element combine with 16 parts of oxygen. The specific heat of copper is 0.095.

$$\text{Hence, } 6.4 / 0.095 = 67.3$$

Since 67.3 is much nearer 63.6 than 127.2, there can be little doubt that 63.6 is the actual value of the atomic weight of copper. We conclude, therefore, that 63.6 grams of copper contains the same number of atoms as 16 grams of oxygen. To make the oxide, in which the combining weights are in the ratio of 63.6 to 16, one atom each of copper and oxygen combine. In the other oxide, two atoms of copper must combine with one of oxygen.

3 Method Involving the Analysis of Gram-Molecular Weights of Compounds of the Element

A more general method of determining atomic weights depends upon determinations of the molecular weights of different compounds of the element. We have defined an atom as the smallest portion of an element that participates in a chemical reaction, and we have found evidence to indicate that a molecule of a compound contains one or more atoms of each of its constituent elements. Therefore, it is evident that a gram-molecular weight of any compound of an element contains one, two, three, or some whole number of gram-atomic weights of that element. If the smallest weight of an element ever found in a gram-molecular weight of any of its compounds can be determined, this weight will be the gram-atomic weight of the element.

Hence this method involves the analysis of as many compounds of an element as possible, with the view of determining the weight of the element in a gram-molecular weight of each. The different weights of the elements found in these analyses will be multiples of some relatively small weight, which is the atomic weight. See Table 5.

As an example of the use of this method, let us consider the atomic weight of chlorine. The gram-molecular weights of several compounds of this element, and the number of grams of chlorine in one gram-molecular weight of each, are shown in the table below.

COMPOSITION OF COMPOUNDS OF CHLORINE

Compounds	Molecular Weight (grams)	Wt of Cl in Molecular Wt (grams)
Hydrogen chloride	36.468	35.46
Chlorine dioxide	67.46	35.46
Phosphorus trichloride	137.41	106.38
Carbon tetrachloride	153.84	141.84
Phosphorus pentachloride	208.33	177.30
Mercurous chloride	472.12	70.92
Mercuric chloride	271.52	70.92

An inspection of the weights of chlorine (third column) reveals that they are either 35.46 g. or

TABLE 5
Determination of Atomic Weights

Substance	Molecular Weight (grams)	Weight of Element in Molecular Weight of Compound (grams)							Formula of Compound
		O	H	Cl	S	P	C	Hg	
Mercurous chloride	472.12			70.92				401.2	Hg ₂ Cl ₂
Mercuric chloride	271.52			70.92				200.6	HgCl ₂
Oxygen	32	32							O ₂
Water	18.016	16	2.016						H ₂ O
Carbon dioxide	44	32					12		CO ₂
Carbon monoxide	28	16					12		CO
Hydrogen chloride	36.468		1.008	35.46					HCl
Phosphorus trichloride	137.41			106.38		31.03			PCl ₃
Phosphorus pentoxide	284.12	160				124.12			P ₂ O ₅
Methane	16.032		4.032				12		CH ₄
Carbonyl chloride	98.92	16		70.92			12		COCl ₂
Carbon disulfide	76				64		12		CS ₂
Chlorine	70.92								Cl ₂
Sulfur dioxide	64	32			32				SO ₂
Sulfur oxy-chloride	118.92	16		70.92	32				SOCl ₂
Acetylene	26.016		2.016				24		C ₂ H ₂
Ethane	30.048		6.048				24		C ₂ H ₆
Acetic acid	60.032	32	4.032				24		C ₂ H ₄ O ₂
Propane	44.064		8.064				36		C ₃ H ₈

multiples of this quantity, 70.92, for example, is 2×35.46 . If the data are sufficient, we may conclude that 35.46 is the atomic weight of chlorine. We cannot be certain that this number is correct until we have analyzed several other compounds of the element. As a matter of fact, the weight of chlorine in gram-molecular weights of all its known compounds is 35.46 g. or a multiple of this quantity, which, therefore, can safely be regarded as the true gram-atomic weight.

Similarly, the analyses of carbon compounds show that the weight of carbon in the gram-molecular weight of any of these is 12 g. or some multiple of 12 g., hence, the atomic weight of carbon is 12. If the weight of carbon in the gram-molecular weight of some of its compounds had been found to be 18 or 30 g., we should have had to conclude that the atomic weight is more likely 6 than 12. If 9 g. of carbon were found in a gram-molecular weight of some compound of this element, an atomic weight of 3 would be indicated. All data, however, indicate that the real atomic weight of carbon is 12.

Some elements do not form many compounds that are easy to make, to purify, and to study, hence, it is possible that, among the available compounds of such an element, there may be none that contains just one gram-atomic weight in a gram-molecular weight, or one atom in a molecule. If we should find, for example, that the molecular weights of compounds of element *X* contain 42, 63, and 84 parts of *X*, and if no other data were available, we should not be justified in concluding that the atomic weight of *X* is the smallest weight (42), for 63 is not a multiple of 42. All of these weights are multiples, however, of 21, hence, until further information was available, 21 would be regarded as a possible value for the atomic weight.

4 Equivalent Weights of the Elements

The methods already described do not give accurate values of the atomic weights. The inaccuracy of the first of these methods is apparent. The second is subject to sources of error in the calculation of molecular weights either from data involving the

weights of definite volumes of gases or from data dealing with the freezing and boiling points of solutions.

A more accurate method involves the *equivalent weights* of the elements. The gram-equivalent weight of an element is the weight of it that *combines* with 1.008 g. of hydrogen or the weight that *can take the place* of this quantity of hydrogen in a compound, it is the weight of the element that is equivalent in *combining capacity* to one gram-atomic weight of hydrogen. Thus, the gram-equivalent weight of oxygen is the weight — 8 g. — that combines with 1.008 g. of hydrogen. Likewise, for chlorine in hydrogen chloride it is 35.46 g. The equivalent weight of any other element can be calculated as the weight of it that combines with 8 g. of oxygen or with 35.46 g. of chlorine. That weight of the element is equivalent to 1.008 g. of hydrogen in its combining capacity — it combines with the same weight of oxygen as 1.008 g. of hydrogen does, and, in a sense, it takes the place of this quantity of hydrogen in compounds with other elements. In general, the equivalent weight of an element is the weight of it that combines with the equivalent weight of *any* other element. Equivalent weights, as a rule, can be determined with greater accuracy than molecular weights, because they involve only simple measurements of weight by means of the balance.

5 Atomic Weights from Equivalent Weights

The principle upon which this method depends may be explained as follows. Let us remember, first, that the gram-equivalent weight of an element combines with, or takes the place of, one gram-atomic weight of hydrogen. Now one atom of hydrogen never combines with more than one atom of another element, but one atom of some elements combines with one of hydrogen, for other elements, one atom combines with two of hydrogen; and for others, three or four atoms of hydrogen are required. These differences are illustrated in such compounds

as HCl , H_2O , NH_3 , and CH_4 . Therefore, for some elements, such as chlorine, the equivalent weight is the same as the atomic weight, a whole atomic weight of chlorine is required to combine with an atomic weight of hydrogen. For oxygen, and certain other elements, the equivalent weight is one half the atomic weight, because a whole atomic weight of oxygen combines with two atomic weights of hydrogen. For nitrogen in ammonia, NH_3 , the equivalent weight is one third of the atomic weight, and for carbon in methane, CH_4 , it is one fourth. We note, therefore, that the atomic weight is equal to the equivalent weight, or it is two, three, four, or some whole number times as great, in the compounds of some elements, the atomic weight may be five, six, seven, or even, for a few elements, eight times the equivalent weight. Hence,

$$\frac{\text{atomic weight}}{\text{equivalent weight}} = \text{a small, whole number}$$

If the equivalent weight and the number indicated in this equation are known, the exact atomic weight can be calculated by multiplying these two quantities, one by the other. The number can be determined by dividing the *approximate* atomic weight, as determined by one of the methods first described, by the equivalent weight and selecting the *whole* number that is nearest the number thus obtained. Thus, if the equivalent weight of a hypothetical element were found to be 10, and the atomic weight as roughly calculated were known to be 32, then it would be evident that the *exact* atomic weight divided by the equivalent weight should give the number 3, and the only reason it does not is that 32 is not the exact value of the atomic weight. To calculate the exact value, we may now multiply the equivalent weight, 10, by 3 which gives 30.

6. An Example of the Calculation of an Exact Atomic Weight

The calculation of the atomic weight of an

element from its equivalent weight is illustrated by the following example. We know that the atomic weight of sulfur is somewhere near 32 from the fact that the weights of sulfur in the molecular weights of its compounds are (approximately) multiples of 32. The equivalent weight of sulfur can be determined from its combination with any one of a number of elements. We find, for example, that the combining ratio of sulfur and silver is one part of sulfur to 6.73 parts of silver. Now the equivalent weight of silver is 107.88, since this weight (in grams) combines with 8 g of oxygen to form silver oxide and with 35.46 g of chlorine to form silver chloride. The weight of sulfur, therefore, that combines with an equivalent weight of silver is

$$107.88 / 6.73 \times 1 = 16.03 = \text{the equivalent weight of sulfur}$$

The equivalent weight (16.03) of sulfur is, therefore, one half of the atomic weight, which is already known to be about 32. Hence,

$$\frac{\text{exact atomic weight of sulfur}}{16.03} = 2$$

$$\text{The exact atomic weight} = 16.03 \times 2 = 32.06.$$

COMBINING CAPACITY OR VALENCE

In Chapter 4 we discussed the combining capacities and the valence numbers of different kinds of atoms in relation to their structures. At that time, it was stated that the valence number of an element depended upon the number of electrons that the atoms of that element lost, gained or shared in reactions with the atoms of other elements. However, the valence numbers of the elements were calculated from chemical data long before anything was known concerning atomic structures. Indeed, information concerning valence contributed no small part to the working out of theories concerning the arrangement of electrons in the different groups, or levels, of the atom. Chemical methods of calculating valence numbers are therefore worthy of our consideration. The structure of an atom may be very useful in helping us to predict the chemical behavior

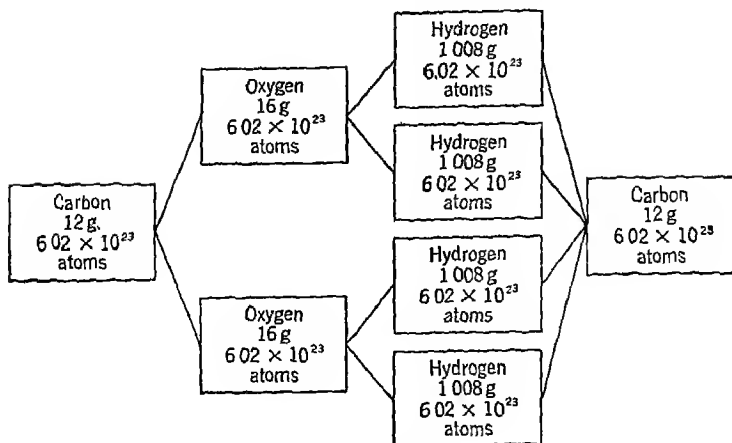


Figure 72 Valence

One atomic weight of carbon combines with two atomic weights of oxygen or four atomic weights of hydrogen. One atomic weight of oxygen combines with two atomic weights of hydrogen. Refer now to Figure 73

of that atom, but is not always enough, in itself, to enable us to find the number of electrons that a chlorine atom shares with oxygen in a particular compound, or to determine whether the valence number of iron in a compound in a test tube is +2 or +3

7 Introduction

In discussing the equivalent weights of the elements, we have pointed out that atomic weights of different elements may combine with one, two, three, or four atomic weights of hydrogen; in other compounds, one atomic weight of an element may combine with as much oxygen, chlorine, or some other element as one, two, three, four, or some other whole number (up to eight) of atomic weights of hydrogen. The atoms of different elements, therefore, may possess different *combining capacities*, or *valence numbers*

The valence of an element is expressed by a small, whole number. The valence number of hydrogen is fixed arbitrarily as 1. Since one atomic weight of chlorine, in hydrogen chloride, combines with an atomic weight of hydrogen, and since the atomic weights of all elements contain the same number of atoms, it is evident that *one atom* of chlorine combines with *one atom* of hydrogen. The

chlorine atom in this compound has, therefore, the same combining capacity as the atom of hydrogen, and the valence number of chlorine is one — the same as the valence of hydrogen

8. The Valence Numbers of Carbon in Carbon Dioxide and of Nitrogen in Ammonia

In carbon dioxide 12 g of carbon is combined with 32 g of oxygen — one gram-atomic weight of carbon and two gram-atomic weights of oxygen. Since the gram-equivalent weight of oxygen is 8 g, that of carbon must be 3 g, or one fourth of the atomic weight. In this particular compound with oxygen, a whole atomic weight of carbon has the same combining capacity as

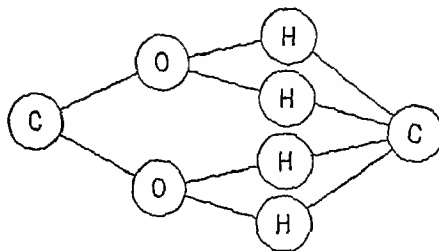


Figure 73 Valence

One atom of carbon must combine with two atoms of oxygen or with four atoms of hydrogen. One atom of oxygen combines with two atoms of hydrogen. Valence of hydrogen=1, valence of oxygen=2, valence of carbon=4

four atomic weights of hydrogen; a single carbon atom, therefore, combines with as much oxygen as four atoms of hydrogen. As compared with 1 for hydrogen, the valence number of carbon in carbon dioxide is 4.

In ammonia, NH_3 , one atomic weight of nitrogen is combined with three atomic weights of hydrogen; hence one atom of nitrogen has the same combining capacity as three atoms of hydrogen, and the valence number of nitrogen in this compound is 3.

9. The Valence Numbers of Other Elements

The valence numbers of other elements can be calculated in a manner similar to that used for carbon, oxygen, nitrogen, and chlorine. The general equation upon which these calculations are based is

$$\text{valence number} = \frac{\text{atomic weight}}{\text{equivalent weight}}$$

As explained for carbon, for example, the use of this equation depends upon the fact that it allows us to calculate the number of atomic weights of hydrogen that one atomic weight of an element combines with or the number of atomic weights of hydrogen to which one atomic weight of the element is equivalent in combining with other elements. By its use, therefore, we are able to make a direct comparison of the combining capacity of an atom of any element with that of an atom of hydrogen.

SOME EXPERIMENTAL METHODS BY WHICH VALENCE NUMBERS ARE DETERMINED

10. Valence Numbers of Metals in Their Compounds with Chlorine or Oxygen

In comparing the valence numbers of different elements, we cannot secure individual atoms for our experiments. Instead we must deal with an equal number of atoms of the different elements, and this number necessarily must be very large. Since the atomic weights (usually expressed in grams) of all elements contain the same number of atoms,

we may be assured that we are dealing with equal numbers if we use the same number of gram-atomic weights, or the same fraction of an atomic weight, of different elements. Thus, the gram-atomic weights of sodium, magnesium, and aluminum are 23 g, 24.32 g, and 27 g, respectively. These weights of the three elements contain the same number of atoms. This is also true for 10×23 g of sodium, 10×24.32 g of magnesium, and 10×27 g of aluminum, and for 0.1 of 23 g of sodium, 0.1 of 24.32 g of magnesium, and 0.1 of 27 g of aluminum. In fact, any weights of these three elements that are in the same proportion as their atomic weights contain the same number of atoms.

Now none of these metals combine very readily with hydrogen to form hydrides. If they are formed, the hydrides are unstable, and hence are unsatisfactory substances with which to work. All of them do combine readily, however, with chlorine and with oxygen. Small weighed samples of the three metals — say 0.01 gram-atomic weight of each — are allowed to react in an atmosphere of pure chlorine or oxygen. When the reactions are completed, the weight of chlorine or oxygen with which each metal has combined can be determined by weighing the products of the reactions and subtracting the weights of the metals themselves. We must then calculate from these results the weight of each metal that would combine with a whole gram-atomic weight of chlorine (35.46 g) or with 8 g of oxygen; this will be the gram-equivalent weight of the metal. Finally, we must compare the equivalent weight with the atomic weight of each metal in order to find the number of atoms of hydrogen to which one atom of each element is equivalent in combining with chlorine or with oxygen.

The results should show that the (approximate) equivalent weight of sodium is 23, the same as the atomic weight, for magnesium it is 12.16, or one half of the atomic weight, and for aluminum it is 9, or one third of the

atomic weight Hence, in combining with chlorine or oxygen,

One atom of sodium is equivalent to one atom of hydrogen.

One atom of magnesium is equivalent to two atoms of hydrogen

One atom of aluminum is equivalent to three atoms of hydrogen

The valence numbers of sodium, magnesium, and aluminum, therefore, are 1, 2, and 3, respectively When the principles involved are clearly understood, the same results can be secured more quickly by dividing each atomic weight by the corresponding equivalent weight

11. Determination of the Valence Numbers of Metals by Displacement of Hydrogen from Acids

Although the three metals used in the experiment just described do not combine readily with hydrogen, we can compare their combining capacities directly with that of hydrogen in another manner. All of these metals are above hydrogen in the activity, or electrochemical, series, and hence they displace hydrogen (page 107) from acids, such as hydrochloric, HCl , and sulfuric, H_2SO_4 . Instead of determining the number of hydrogen atoms with which one atom of each metal combines, it is possible to determine the number of hydrogen atoms that one atom of each metal *replaces* in reacting with an acid. This method will also show, therefore, the number of hydrogen atoms to which one atom of a metal is equivalent in combining capacity. As before, we must use weights of sodium, magnesium, and aluminum that are in the same proportion as their atomic weights. The weights actually used in the experiment must be very small, since even one gram of hydrogen, if liberated in any of the reactions, would occupy a very large volume, a volume too large to be measured conveniently. Instead of using gram-atomic weights of the three metals, therefore, let us use 0.23 g of sodium, 0.243 g of magnesium, and 0.270 g of aluminum. These weights of the metals are slipped beneath the mouths of three tubes which have been filled with dilute hydrochloric acid and inverted in vessels containing the same solution. The hydrogen liberated in each tube displaces the solution

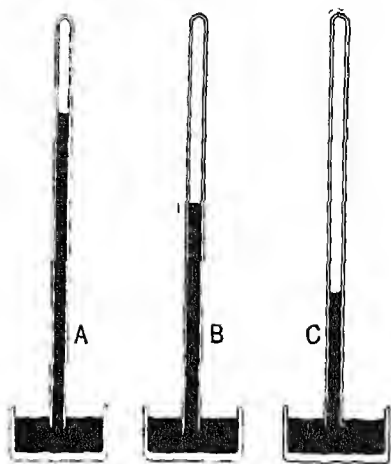


Figure 74 The Displacement of Hydrogen from Hydrochloric Acid by Sodium (A), Magnesium (B), and Aluminum (C)

and is collected in the upper part of the tube (Figure 74). The relative capacities of the three metals to replace hydrogen, and hence their valence numbers, can be determined by comparing the volumes of hydrogen that collect in the three tubes. These volumes are in the order of 1, 2, and 3 for sodium, magnesium, and aluminum, respectively. Equal volumes of hydrogen (under the same conditions) contain the same number of molecules, and also the same number of atoms. It is evident, therefore, that the numbers of hydrogen atoms replaced by single atoms of the three metals are also in the order of 1 for sodium, 2 for magnesium, and 3 for aluminum. This does not mean, necessarily, that one atom of sodium replaces one atom of hydrogen, one atom of magnesium replaces two atoms of hydrogen, and one atom of aluminum three atoms of hydrogen. To verify these replacement values, it is necessary to convert the *volumes* of hydrogen displaced in the three tubes into *weights* of hydrogen, and then to compare these weights with the atomic weight of hydrogen. When this is done the weights of hydrogen are found to be (approximately)

0.01 g of hydrogen for 0.230 g of sodium,
0.02 g of hydrogen for 0.243 g of magnesium,
0.03 g of hydrogen for 0.270 g of aluminum

If gram-atomic weights of the metals had been used in the experiment, approximately 1, 2, and 3 g of hydrogen would have been liberated in the three reactions. Since 1 g (more exactly 1.008 g)

of hydrogen contains the same number of atoms as 23 g of sodium, 24.32 g of magnesium, and 27 g of aluminum, it is evident, therefore that

1 atom of sodium replaces 1 atom of hydrogen
 1 atom of magnesium replaces 2 atoms of hydrogen
 1 atom of aluminum replaces 3 atoms of hydrogen

DIFFERENT VALENCE NUMBERS OF AN ELEMENT

At one time, it was believed that the valence number of any element is always the same. This idea probably was based upon Dalton's belief that all of the atoms of an element were identical in every respect.

The fact that two elements may form more than one compound, however, means that one of these elements has different equivalent weights in these compounds. The equivalent weight of sulfur in SO_2 is 8, in SO_3 it is $5\frac{1}{8}$, and in H_2S it is 16. In the five oxides of nitrogen (page 39), the equivalent weights of nitrogen are 11, 7, $12\frac{1}{3}$, $3\frac{1}{2}$, and $2\frac{1}{6}$, respectively. Carbon forms two oxides, CO and CO_2 . Iron forms compounds in which its valence number is 2 and others in which its valence number is 3. Manganese has five different valence numbers: 2, 3, 4, 6, and 7. Similar variations occur for many other elements, such as phosphorus, chlorine, bromine, iodine, chromium, mercury, tin, lead, and copper. On the other hand, several elements display only one valence number. Among these are sodium, potassium, calcium, aluminum, and magnesium.

Each element forms as many different classes of compounds as it has valence numbers. In order that the compounds of one class may be changed into those of another, the valence of the element must be changed; that is, the element must be oxidized or reduced. The compounds of one class, however, are usually closely related and can be changed one into another by simple reactions such as double decomposition. For example, all the soluble compounds of ferrous iron (valence number, 2) react with sodium hydroxide to form white ferrous hy-

droxide, $\text{Fe}(\text{OH})_2$, and with potassium *ferricyanide*, $\text{K}_3\text{Fe}(\text{CN})_6$, to form a dark blue precipitate of $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$. Ferric compounds, in which the valence number of iron is 3, react with sodium hydroxide to form red ferric hydroxide, $\text{Fe}(\text{OH})_3$, and with potassium *ferrocyanide*, $\text{K}_4\text{Fe}(\text{CN})_6$, to form a blue precipitate of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$.

The suffixes *-ous* and *-ic* are used to distinguish between two classes of compounds in which a metal has two valence numbers. We should not speak of iron chloride or mercury sulfide, for example, since these names do not designate any specific substance. But when we use the term *ferrous chloride*, it is at once clear that we mean FeCl_2 and not FeCl_3 . Similarly, we must speak of mercurous sulfide, Hg_2S , or mercuric sulfide, HgS . The suffixes *-ous* and *-ic* serve very well for compounds of the metals — sulfides, chlorides, sulfates, nitrates, and so on, since the metal seldom has more than two valence numbers in such compounds. In the oxides and other compounds of the non-metals there is a greater variation in valence, four valence numbers of chlorine are represented in the oxygen compounds of that element, NaClO , NaClO_2 , NaClO_3 , and NaClO_4 . The terminology employed for compounds such as these will be discussed on page 160.

Review Exercises

- 1 The specific heat of a solid element is 0.032. Calculate the atomic weight of this element by applying the method of Dulong and Petit.
- 2 From the data contained in the table on page 131, select the approximate atomic weight of each of the elements in the list.
- 3 Define equivalent weight and explain how the equivalent and atomic weights can be used to determine the valence numbers of the elements.
- 4 Describe a method of determining the accurate values of atomic weights.
- 5 The approximate atomic weight of the metal x appears to be 58. Experiment shows that 1 gram of x combines with 1.2084 grams of

- chlorine. What is the actual atomic weight of x ?
- 6 A compound containing phosphorus and chlorine is composed of 22.5 per cent of phosphorus. The molecular weight of the compound is 137.5 g. What is the valence number of phosphorus in this compound and what is the formula of its chloride?
7. The percentage compositions of two oxides of chromium are
- | | | | |
|--------|-----|--------|-------|
| (1) Cr | 52% | (2) Cr | 68.4% |
| O | 48% | O | 31.6% |
- (a) Calculate the equivalent weight of chromium in each compound.
- (b) Calculate the valence number of chromium in each compound.
- (c) The equivalent weight of chromium in (2) is found, by a more accurate determination than that indicated, to be 17.34. Calculate the atomic weight of the element.
- 8 Calculate, from the formulas, the weight of 1 liter (standard conditions) of each of the following gases: hexane, C_6H_{14} ; acetylene, C_2H_2 ; ammonia, NH_3 ; hydrogen sulfide, H_2S ; and sulfur dioxide, SO_2 .
- 9 By reacting with hydrochloric acid, 0.327 g of a metal displaces 112.0 ml of hydrogen (under standard conditions). What is the valence number of the metal? The atomic weight of the metal is 65.4.
- 10 With what weight of oxygen will the same weight of the metal mentioned above combine?
- 11 If Dalton's formula for water, HO , were correct, what would be the valence number of oxygen? How do we know that the valence number of oxygen is 2?
- 12 If the valence number of aluminum is 3 and its atomic weight is 26.97, what (standard) volume of hydrogen will be liberated when 10 g of aluminum reacts with hydrochloric acid?
- 13 One gram-molecular weight of a compound of element x and hydrogen contains one gram-atomic weight of x and one and one-half times as much hydrogen as is contained in a gram-molecular weight of water. What is the valence number of x ?
- 14 Gram-molecular weights of compounds of the hypothetical element E contain 21, 49, and 70 grams, respectively, of E . What is the largest number that might be the atomic weight of E on the basis of these data? How would your answer be changed if analyses of other compounds showed 7, 10.5, and 35 grams of E in gram-molecular weights of three compounds?
- 15 Define atomic weight, equivalent weight, specific heat, valence, valence number of an element.
- 16 Which elements are oxidized and which are reduced in the following reactions?
- $$Mg + H_2O \longrightarrow MgO + H_2$$
- $$2FeCl_2 + SnCl_4 \longrightarrow 2FeCl_3 + SnCl_2$$
- $$H_2S + I_2 \longrightarrow 2HI + S$$
- 17 In terms of the changes in the valence numbers of elements, define (1) oxidation and (2) reduction. Explain by appropriate illustrations.
- 18 How are valence numbers of 1 for sodium, 2 for magnesium, and 3 for aluminum explained in terms of the structures of the three kinds of atoms?
- 19 If the equivalent weight of a metal is one third of the metal's atomic weight, what (standard) volume of hydrogen will be liberated when one fourth of the gram-atomic weight of the metal reacts with hydrochloric acid?
- 20 The number of atoms of hydrogen with which one atom of an element will combine, or the number of hydrogen atoms that one atom of an element can replace, can be calculated by dividing the element's atomic weight by its equivalent weight. Why is this true?

References for Further Reading

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- Moore, F. J., *History of Chemistry*
- Atomic Weights: *J. Chem. Ed.*, 9, 453 (1932), 11, 441 (1934)
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SYMBOLS, FORMULAS, AND EQUATIONS

1. Introduction

This chapter explains the chemist's language — the symbols, formulas, and equations that he uses in place of words to express certain facts concerning substances and the chemical changes in which they engage. He uses them, not to conceal his information in strange and mystical forms as the alchemist did, but because they are simple and convenient forms of expression. Wherever chemistry is discussed, we find them widely used, one must understand them, therefore, if one is to understand the literature of the science.

2. Symbols of the Elements

The symbols of the elements are the initials or abbreviations of their names, usually the English name is abbreviated, but sometimes the Latin name is used. Thus, H, O, Cl, N, Br, P, S, Al, Mg, and Ca are the symbols respectively of hydrogen, oxygen, chlorine, nitrogen, bromine, phosphorus, sulfur, aluminum, magnesium, and calcium. The symbol of iron is Fe, which is taken from the Latin word *ferrum*. The following symbols also have Latin origin: Au, from *aurum*, for gold; Ag, from *argentum*, for silver; Pb, from *plumbum*, for lead; Sn, from *stannum*, for tin. Na and K, the symbols of sodium and potassium, respectively, are from the German words *natrum* and *kalium*. Not only does the symbol represent the element in general, but it indicates a very definite weight of the element. When we write H_2 , for example, we refer to a gram-

molecular weight (2.016 g). The symbol H refers to one gram-atomic weight of the element.

3. Formulas

The composition of a compound can be expressed conveniently by placing together the symbols of the elements that compose it. Such a statement of the composition of a compound is called a *formula*. The symbol of each element must occur as many times in the formula of the compound as there are atomic weights of the element in a molecular weight of the compound, or — in other words — as many times as there are atoms of the element in a molecule of the compound. The number of atoms (unless that number is one) of an element occurring in a molecule is indicated by a figure written as a subscript below and to the right of the symbol of the element. Thus, the formula for carbon dioxide, CO_2 , indicates that a molecule of carbon dioxide contains one atom of carbon and two atoms of oxygen.

The formula of a *compound composed of molecules* (page 57) states the following facts about the compound:

- (1) The elements of which it is composed. CO_2 , for example, is composed of carbon and oxygen.
- (2) The number of atoms of each element in a molecule of the compound. The molecule CO_2 contains one atom of carbon and two of oxygen.
- (3) The ratio of the weights of any two elements in the compound. The compound CO_2 contains two atomic weights of oxygen for

each atomic weight of carbon, the ratio of the weights of the two elements is 32 to 12. In glucose, $C_6H_{12}O_6$, the ratio of the weights of carbon and oxygen is 72 to 96.

- (4) The molecular weight of the compound. This is numerically equal to the sum of the atomic weights of the constituent elements, each atomic weight being taken as many times as there are atoms of that element in a molecule of the compound.

The molecular weight of carbon dioxide, CO_2 , is $12 + (2 \times 16) = 44$.

For compounds composed of ions instead of molecules, the formula shows the relative number of each ion and the simplest complete set of ions in the compound. Thus, the formula Na^+Cl^- shows that for each sodium ion in sodium chloride there is one chloride ion. There are no molecules of such compounds, but we sometimes refer to the relative weight corresponding to the formula, e.g., Na^+Cl^- , as the molecular weight, more accurately, it is the *formula weight*. The gram-formula weight of sodium chloride is $23 + 35.46 = 58.46$ g. This weight of salt contains the same number of sodium and also the same number of chloride ions as there are atoms of oxygen in 16 g. of that element.

DERIVATION OF FORMULAS

The formula of a compound can be derived if the following information is available: (1) the elements that compose the compound, (2) their atomic weights, and (3) the molecular weight and percentage composition of the compound. In the paragraphs that follow we shall show how this information is used to determine, first, the formula of a compound composed of molecules, in which atoms share electrons, and secondly, the formula of a compound composed of ions. In general, the method is the same for the determination of both formulas, except that the weight corresponding to the simplest possible formula, or complete set

of ions, must be used for ionic compounds, instead of the molecular weight.

4. Derivation of the Formula of Water — a Compound Composed of Molecules

When a compound is analyzed, the results are usually stated as the percentages of the different elements in the compound. Percentage means parts per hundred. Hence, if we find that the percentage of hydrogen in water is 11.19, this means that 11.19 g. of every 100 g. of water consists of hydrogen. The percentage of oxygen in water is 88.81. Knowing the percentage composition of water, we might write the statement, $H_{11.19}O_{88.81}$, to express the ratio of the *weights* of the two elements that combine. The *formula*, however, must show the relative number of *atoms* of each element in the compound, it must show, for example, whether two atoms or only one atom of hydrogen combines with each atom of oxygen. To obtain this information, we can divide the weights representing the percentages of the different elements by the atomic weights of the elements. Thus, we divide 11.19 by 1.008 and 88.81 by 16.

$$\frac{11.19}{1.008} = 11.10 = \text{number of atomic weights of hydrogen in 100 parts of water}$$

$$\frac{88.81}{16} = 5.55 = \text{number of atomic weights of oxygen in 100 parts of water}$$

The formula might now be written as $H_{11.10}O_{5.55}$, or as $H_{11.10 \times 1.008}O_{5.55 \times 16}$ to show that 11.10 atomic weights of hydrogen combine with 5.55 atomic weights of oxygen. Since atomic weights of all elements contain the same number of atoms, this formula also shows that *atoms of hydrogen and oxygen are combined in the ratio of 11.10 to 5.55*.

In a molecule of water the numbers of atoms of hydrogen and oxygen must be in a ratio of two small, *whole* numbers, such as one to one or two to one, and not 11.10 to 5.55, molecules contain whole numbers of atoms, not fractions. Our problem, how-

ever, is almost solved. We may reason as follows.

Hydrogen and oxygen atoms combine in the ratio of 11.10 to 5.55

How many atoms of hydrogen combine with 1 atom of oxygen?

$$\text{The answer is } \frac{11.10}{5.55} = 2$$

The molecule of water, therefore, contains two atoms of hydrogen for each atom of oxygen, and the formula can be written as H_2O .

5. Actual Molecular Formulas

The formula, H_2O , which has just been derived for water is the *simplest* possible formula, it shows only the ratio in which the two kinds of atoms combine and are present in the molecule. However, the actual formula corresponding to the molecule of water might be H_4O_2 , H_6O_3 , etc., in each of which, as in H_2O , there are two atoms of hydrogen for each atom of oxygen.

To determine the formula actually representing a molecule, it is necessary to know the molecular weight of the substance. For water in the vapor state, the gram-molecular weight—the weight of 22.4 standard liters—is 18.016 g. The correct molecular formula for water, therefore, is H_2O , because 18.016 is the sum of one atomic weight of oxygen (16) and two atomic weights of hydrogen (2×1.008). If the molecular weight had been found to be 36.032, the formula would have been H_4O_2 ; if 54.048, the formula would have been H_6O_3 , and so on.

But the fact that the formula of water, or of another substance, is known for the vapor state does not mean that the formula is the same for the substance in its liquid and solid states. The formula H_2O represents the molecule of water vapor, but there are indications of the existence of $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$, or H_4O_2 and H_6O_3 , molecules in the liquid.

6. Derivation of the Formula of Sodium Sulfate — a Compound Composed of Ions

Let us determine, next, the formula of a substance that is a little more complex than water and is composed of ions instead of molecules. A certain compound is found, by analysis, to have the following composition: sodium, 32.38 per cent, sulfur, 22.57 per cent, and oxygen, 45.05 per cent. These percentages indicate that 100 g. of the compound contains 32.38 g. of sodium, 22.57 g. of sulfur, and 45.05 g. of oxygen.

Let us now divide the weights mentioned above by the atomic weights of the corresponding elements in order to determine the number of gram-atomic weights of each element that is present in 100 g. of the compound.

$$\frac{32.38}{23} = 1.408, \quad \frac{22.57}{32} = 0.704;$$

$$\text{and } \frac{45.05}{16} = 2.816$$

Since there are equal numbers of atoms in equal numbers of atomic weights, the atoms of sodium, sulfur and oxygen must be combined in this compound in the proportion of 1.408, 0.704 and 2.816. Hence for each atom of sulfur there must be $\frac{1.408}{0.704} = 2$ atoms of sodium and $\frac{2.816}{0.704} = 4$ atoms of oxygen.

The simplest formula of this compound, therefore, is Na_2SO_4 , and its name is sodium sulfate. It is composed of ions, $2\text{Na}^+ + \text{SO}_4^{2-}$. The formula that we have just derived corresponds to a complete set of ions, two of sodium for each sulfate ion.

7. Percentage Composition Calculated from the Formula

Since the formula shows the relative number of atomic weights of each element in the compound, it provides all the data required for the calculation of the percentage of each element in the compound. To find the per-

centage composition of sodium sulfate, for example, we first add together the atomic weights of sodium, sulfur, and oxygen, taking the atomic weight of each as many times as there are atoms of the element in the formula of the compound.

$$(2 \times 23) + 32 + (4 \times 16) = 142$$

Of 142 g of the compound, 46 g is sodium, 32 g is sulfur, and 64 g is oxygen. Then of 100 g of the compound,

$$\begin{aligned} 46/142 \times 100 &= 32.38 \text{ g of sodium,} \\ 32/142 \times 100 &= 22.57 \text{ g of sulfur,} \\ \text{and } 64/142 \times 100 &= 45.05 \text{ g of oxygen} \end{aligned}$$

Since percentage means parts per hundred, the percentages of sodium, sulfur, and oxygen are 32.38, 22.57, and 45.05, respectively.

8 The Use of Valence Numbers in Writing Formulas

The formula of a compound is correctly expressed only when the sum of the valence numbers of those atoms or ions having positive valence numbers equals the sum of the valence numbers of those having negative numbers. Thus, in the formula of aluminum oxide, Al_2O_3 , the sum of the valence numbers of the two atoms of aluminum is +6 and that of the three atoms of oxygen is -6. If this relation did not hold, the combining capacities of the two kinds of atoms would not be balanced, and the formula would not be correct. Since the valence number of chlorine is -1, three atoms of chlorine are required to balance the combining capacity of one atom of aluminum, and hence, the formula of aluminum chloride is AlCl_3 . Similarly, three atoms of chlorine are required for each atom of iron in ferric chloride, FeCl_3 , but only two atoms of chlorine are required per atom of iron in ferrous chloride, FeCl_2 , in which iron's valence number is +2.

The valence number of oxygen is -2. One atom of calcium which has a valence number of +2 reacts with one atom of oxygen to form calcium oxide, CaO . In a simi-

lar manner we can easily determine the formula of any oxide if we know the valence number of the element that combines with oxygen. For example, sodium has a valence number of +1, and hence the formula for sodium oxide is Na_2O , because two sodium atoms are required to balance the combining capacity of one atom of oxygen. The formulas of the oxides of magnesium, lead, mercury, cadmium, and iron, in which the metals have a valence number of +2, are MgO , PbO , HgO , CdO , and FeO , respectively. The formulas of the oxides of elements having other valence numbers are illustrated by the following examples in which the valence numbers of the elements combining with oxygen are shown by the numbers placed above and to the right of the symbols of the elements: Si^{+4}O_2 , $\text{N}_2^{+5}\text{O}_5$, Cr^{+6}O_3 , $\text{Cl}_2^{+7}\text{O}_7$, $\text{O}_6^{+8}\text{O}_4$.

9. Compounds in which Valence Numbers Appear to be Abnormal

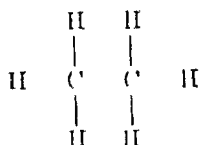
The valence number of an element or of a radical is always a small, whole number. There are some compounds, however, for which the rule does not appear to hold. For example, the formula for magnetic iron oxide is usually written Fe_3O_4 , in which the valence number of iron appears to be $2\frac{2}{3}$, this cannot, of course, be the true valence number. This compound probably contains iron in two valence conditions, two oxides, FeO and Fe_2O_3 , are combined in this compound, and iron has two valence numbers, 2 and 3. The formula, then, may be regarded as $\text{Fe}(\text{FeO})_2$.

The valence number of lead in red lead, Pb_3O_4 , also appears to be $2\frac{2}{3}$, but this, too, is an unusual compound. Its composition is probably $2\text{PbO} \cdot \text{PbO}_2$, or Pb_2PbO_4 , in which the valence numbers of lead are 2 and 4, respectively. In sodium peroxide, Na_2O_2 , and in hydrogen peroxide, H_2O_2 , the valence number of both sodium and hydrogen appears to be 2, but is actually only 1. The structure of hydrogen peroxide is probably



It contains the O^- radical, which, with a valence number of -2 , requires two atoms of hydrogen.

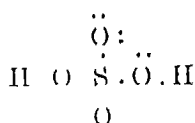
The valence number of carbon in many organic compounds must also be explained in a similar manner, i.e., in terms of structure and the arrangement of atoms within the molecule. The formula for ethane, for example, is C_2H_6 , this formula indicates for carbon a valence number of 3, which is not in accordance with other evidence concerning the valence of this element. The correct valence number for carbon is 4, as shown by the arrangement of atoms in the ethane molecule



One of the valence-units (one electron) of each carbon atom unites that atom to the other carbon atom, the other three unite carbon and hydrogen. Formulas of this kind, which show how atoms are arranged within the molecule as well as the number of atoms of each element, are called *structural formulas*.

10. The Valence Numbers of Radicals and Ions

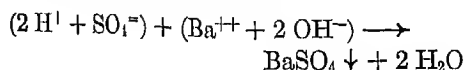
Radicals are groups of atoms that act together as a unit in many chemical changes. *Most of the radicals with which we are concerned at this time are ions.* They are found in ionic compounds such as sodium sulfate, Na_2SO_4 , and in aqueous solutions of such substances. Many of them are found in acids, also. In the pure acids, the radicals do not exist, usually, as ions, in sulfuric acid, for example, the two hydrogen atoms share electrons with two oxygen atoms of the sulfate radical, SO_4 , and the whole structure, H_2SO_4 , is a molecule rather than a group of ions:



These groups do exist, at least in part, as ions in aqueous solutions of acids. Thus the sulfate groups exist as ions in crystals

of metallic sulfates, like sodium sulfate ($2 Na^+ + SO_4^{--}$), and in solutions of such compounds and also in solutions of sulfuric acid.

In many of the reactions that involve sulfuric acid (hydrogen sulfate) or any other sulfate, such as sodium sulfate, the sulfate ion or radical is not changed, it is only transferred from one compound to another. For example, when a solution of sulfuric acid is mixed with a solution of barium hydroxide, the following reaction occurs



Barium sulfate, $BaSO_4$, is only very slightly soluble, and therefore it precipitates. The same substance is formed when any soluble sulfate and any soluble barium salt (barium chloride, $BaCl_2$, for example) are mixed. Hence, the sulfate radical or ion has the same characteristics and valence number, regardless of the compound from which it is derived; the properties of the sulfate ion derived from sulfuric acid are the same as those of the ion from sodium sulfate, magnesium sulfate, or any other sulfate. The same can be said for other radicals.

Since one nitrate radical combines with one atom of hydrogen in nitric acid, it is evident that its valence number is -1 . Similarly, the sulfate radical (SO_4) in sulfuric acid (H_2SO_4) has a valence number of -2 . The phosphate radical (PO_4) in phosphoric acid (H_3PO_4) has a valence number of -3 . The following list contains the formulas and names of several acids and salts that contain radicals. The student is advised to inspect these with the view of determining (from the formula) the valence number of each radical.

H_3AsO_3	Arsenous acid or hydrogen <u>arsenite</u>
Na_2AsO_3	Sodium <u>arsenite</u>
H_3AsO_4	Arsenic acid or hydrogen <u>arsenate</u>
Na_2AsO_4	Sodium <u>arsenate</u>
$HClO$	Hypochlorous acid or hydrogen <u>hypochlorite</u>
$Ca(ClO)_2$	Calcium <u>hypochlorite</u>

HClO_2	Chlorous acid or hydrogen <u>chlorite</u>
KClO_2	Potassium <u>chlorite</u>
HClO_3	Chloric acid or hydrogen <u>chlorate</u>
$\text{Ba}(\text{ClO}_3)_2$	Barium <u>chlorate</u>
HClO_4	Perchloric acid or hydrogen <u>perchlorate</u>
KClO_4	Potassium <u>perchlorate</u>
H_3PO_4	Phosphoric acid or hydrogen <u>phosphate</u>
AlPO_4	Aluminum <u>phosphate</u>
KMnO_4	Potassium <u>permanganate</u>
Na_2CrO_4	Sodium <u>chromate</u>
Na_2CO_3	Sodium <u>carbonate</u>
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	Calcium <u>acetate</u>
$\text{Mg}_3(\text{PO}_4)_2$	Magnesium <u>phosphate</u>

All the radicals of the compounds listed above contain oxygen, but this is not true of radicals in general. The group $(\text{Fe}(\text{CN})_6)$, for example, acts as a radical or ion in potassium ferrocyanide $(\text{K}_4\text{Fe}(\text{CN})_6)$. Its valence number is obviously -4 , since one radical combines with four atoms of potassium, each of which has a valence number of $+1$. Other radicals that do not contain oxygen are illustrated by the compounds below. The student is advised to determine the valences of the radicals that are underlined.

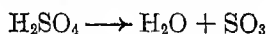
$\text{Na}_3\text{Fe}(\text{CN})_6$	Sodium <u>ferrocyanide</u>
$\text{Na}_2\text{Co}(\text{NO}_2)_6$	Sodium <u>cobaltic nitrite</u>
NH_4Cl	<u>Ammonium</u> chloride
$(\text{NH}_4)_2\text{SO}_4$	<u>Ammonium</u> sulfate
$(\text{NH}_4)_3\text{AsS}_4$	<u>Ammonium</u> <u>sulfoarsenate</u>
K_2PtCl_6	Potassium <u>chloroplatinate</u>
Na_2SiF_6	Sodium <u>fluosilicate</u>
HBF_4	Fluoboric acid or hydrogen <u>fluoborate</u>

11. Explanation of the Valence Numbers of Radicals or Ions

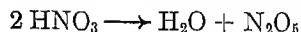
All hydroxides contain the hydroxyl group, OH . In the hydroxides of the metals, such as sodium hydroxide, NaOH , this group exists as the ion, OH^- ; in certain other compounds it is an uncharged radical. The oxygen atom of this radical, or ion, has a valence number of -2 , and the single hydrogen atom's number is $+1$; hence, one valence number, or bond, of oxygen is unsatisfied in

the group, which, therefore, must have a valence number of -1 . The formulas of the hydroxides of *univalent* (valence number, 1) elements contain one hydroxyl group, e.g., NaOH , AgOH . The number of hydroxyl groups in the formulas of the hydroxides of other elements varies with the valence numbers of these elements: $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Cu}(\text{OH})_2$.

The valence numbers of other radicals, or ions, can be explained in a similar manner. The sulfate ion of the metallic sulfates contains four atoms of oxygen, which have a total valence number of -8 . What is the valence number of sulfur? We may answer this question by considering the composition of sulfuric acid and the method by which it is formed from an oxide of sulfur (page 70). To determine the formula of this oxide, let us subtract from the formula of the sulfuric acid molecule, H_2SO_4 , the formulas of as many molecules of water as it is possible to obtain from a molecule of the acid; this is a single molecule since there are only two atoms of hydrogen in a molecule of the acid:



Since the formula of the oxide is SO_3 , the valence number of sulfur must be $+6$. This leaves, then, two oxygen-valences unsatisfied in the SO_4 radical and accounts for the valence number of -2 for this group. Similarly, the valence number of nitrogen in the nitrate radical is $+5$, as can be shown from the formula of nitric acid. If the water (all the hydrogen and an equivalent amount of oxygen) is removed from HNO_3 , N_2O_5 is left:



Since the valence number of nitrogen is $+5$ and the total valence number of the three oxygen atoms in the nitrate group is -6 , one oxygen-valence remains unsatisfied. The valence number of the nitrate radical, therefore, is -1 .

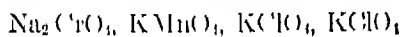
12. The Valence Numbers of Elements in Radicals and Ions

Sometimes it is necessary to determine,

from the formula, the valence number of the middle element — as usually written — in the formula of a compound containing a metal, a non-metal the valence of which we are to determine, and oxygen; as an example, we may refer again to sodium sulfate, Na_2SO_4 . (We cannot use this method for all compounds; see page 142.) The valence number of sulfur is equal to the difference between the total valence number of the third element (oxygen) and the total valence number of the first element (sodium). This difference is

$$(4 \times 2) - (2 \times 1) = 6.$$

The sign of sulfur's valence number is positive, because the positive and negative numbers of the different elements of the compound must balance. Since four oxygen atoms together have a valence number of -8 and two atoms of sodium a combined valence number of $+2$, sulfur's valence number is $+6$. Likewise, the valence number of sulfur in sodium sulfite, Na_2SO_3 , is $+4$. In trisodium phosphate, Na_3PO_4 , phosphorus has a valence number of $+5$. The student is advised to find, in a similar manner, the valence numbers of the elements underlined in the following compounds:



We can accomplish the same results in a slightly different manner. In Na_2SO_4 the valence number of the SO_4 ion is -2 , as indicated by the two ions of sodium required for each sulfate ion in the compound. The four oxygen atoms of the sulfate ion have a combined valence number of -8 , and since the valence number of the ion is only -2 , the valence number of sulfur must be $+6$.

It is often convenient to be able to determine quickly the valence numbers of such elements in the manner indicated. This is particularly important in writing equations for reactions in which these elements undergo changes in valence. For reactions in which no changes of this kind occur, the valence number of the radical or ion

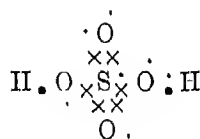
is of greater importance than those of its constituent elements.

13 An Explanation of the Valence Numbers of Elements in Covalent or Molecular Compounds

The explanation of the valence number of an element in compounds formed when the atoms of the element gain or lose electrons offers no difficulty, it depends upon the number of electrons that each atom gains or loses. The valence number of an element in covalent compounds also depends upon the number of electrons that an atom of the element *uses* in forming shared electron pairs with other atoms.

The non-metallic elements in acids containing oxygen — sulfur in H_2SO_4 , for example — are linked, by sharing electrons, with oxygen.

In the formulas that follow we have indicated by \times the electrons belonging originally to the central atom, e.g., sulfur.



An inspection of the above formula shows that the sulfur atom uses all six of its valence, or outermost, electrons — indicated by \times — in forming the bonds, or linkages, with oxygen. Since the oxygen atoms have only 6 (outermost) electrons each, and since two of these oxygen atoms use one electron (\cdot) each in the linkages with hydrogen (\cdot), it is apparent that the sulfur atom must provide six of the eight electrons by which it is bound to oxygen. Hence, the valence number of the sulfur is 6. This is sometimes called the *oxidation number* of sulfur. The oxidation numbers of oxygen and hydrogen in this compound are -2 and 1 , respectively.

Similarly, the valence or oxidation numbers of chlorine in the acids indicated below are 1 , 3 , 5 , and 7 , respectively, because the chlorine atom uses 1 , 3 , 5 , and 7 of its electrons in forming linkages with oxygen.

for iron in $\text{Na}_4\text{Fe}(\text{CN})_6$ is 6, because of the six CN radicals that are attached to the central atom of iron.

The co-ordination number should not be confused with co-ordinate covalence. The atoms or radicals that surround a central atom may be attached by regular covalent bonds or by co-ordinated covalent bonds. In the sulfate ion, for example, the co-ordination number is 4, but not all the pairs of electrons by which oxygen atoms are attached to the sulfur atom are furnished by the sulfur atom. It should also be noted that the valence number and the co-ordination number are not the same; in the sulfate ion, for example the valence number of sulfur is +6, while the co-ordination number is 4.

THE CHEMICAL EQUATION

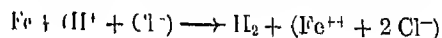
In chemical changes the arrangement of atoms in the molecules or ions of the starting materials is broken up, and the atoms are rearranged in different structural patterns to form the molecules or ions of the products. Since, in accordance with the law of Conservation of Mass, there is no loss or gain in weight, all the atoms present originally must appear in the products. This being the case, it is possible to show the changes that occur by means of statements written, not in words, but in chemical symbols, such a statement is called a chemical equation. It does not have the same meaning as a mathematical equation, it is an equation only in the sense that it shows an equality between the weights, and between the number of atoms of each element, on the two sides of the equation.

16 Information Needed to Write Equations

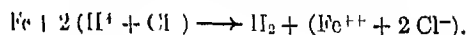
To write a correctly balanced equation we must know the formulas of all the substances involved — those used and those produced — in the reaction. More important still, we must know that the reaction as written is the one that actually occurs, when hydrogen and oxygen react, we must know that the

product is water, H_2O , and not hydrogen peroxide, H_2O_2 .

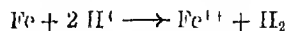
Iron dissolves in a solution of hydrogen chloride (hydrochloric acid), forming hydrogen, which escapes as a gas, and a chloride of iron. These facts are not sufficient to indicate the correct equation for this reaction. One must know that hydrogen chloride is represented correctly by the formula HCl and that iron, to the best of our knowledge, exists as Fe , not Fe_2 , Fe_3 , or Fe_4 . One must know, too, that of the two chlorides of iron, FeCl_2 and FeCl_3 , the former (ferrous chloride) is produced in this reaction. When all these facts are known, one can write the equation in a temporary form as follows.



To balance this equation two molecules of HCl are required to supply the two hydrogen atoms and the two chlorine atoms which must be used in forming the products.



In this equation we have written the formula of ferrous chloride as $(\text{Fe}^{++} + 2 \text{Cl}^-)$, to show that the iron and chlorine atoms are electrically charged, and that the substance formed really consists of the ions and not molecules of FeCl_2 . In the solution these ions are separated, but as the water evaporates they will take up definite positions in space and form crystals of ferrous chloride. It is evident that the ions of chlorine undergo no change in this reaction. The change is one that involves only atoms of iron and hydrogen. For this reason, the equation is sometimes written to show the change that they undergo, and the chlorine is omitted.



This equation shows that each atom of iron gives two electrons to hydrogen, one to each of two atoms. This is the whole story.

In the pages that follow, we shall try to write equations that will show the substances that participate in the reactions as nearly as possible in the form in which they exist. Thus, we shall represent sodium chloride in solution as $(\text{Na}^+ + \text{Cl}^-)$ to show that the solution contains these ions, and that the ions are not actually combined with

one another. Ferrous chloride will be represented in solution as $(\text{Fe}^{++} + 2 \text{Cl}^-)$. When the solid forms of these substances are employed, we shall write them as NaCl and FeCl_2 , respectively, to show that the ions are closely associated in definite crystalline patterns. We shall represent substances that are composed of molecules by molecular formulas such as H_2O and CO_2 , since these formulas show the real divisions of such substances to be molecules.

In writing the equation for a reaction between substances in solution, the water in which the reacting substances are mixed is not indicated. It usually takes no direct part in the reaction, and therefore need not be shown.

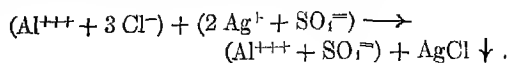
An equation is not a means of determining the course a reaction takes or the products it forms, but a means of stating the change which, by experiment or otherwise, has been observed to occur. The student should not be discouraged at this time if equations offer considerable difficulty. The trouble lies not in the equations themselves, or in the methods that are commonly used to balance them, but in the large number of facts that must be known before a statement concerning a given reaction can be made either in the form of an equation or in words. As your study proceeds, and your experiences in the laboratory expand, the equations that may appear difficult at this time will prove extremely simple.

If the valence numbers of the elements and radicals, or ions, in the compounds are known, the formulas can be written without difficulty, and so, with the help of valence numbers and without further experiment or analysis, we may proceed to write the equations for many reactions. Let us, therefore, next consider the use of valence numbers in writing equations.

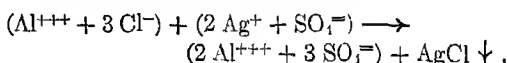
17. The Convenience of Valence Numbers in Writing Equations

As an example of balancing an equation for a reaction involving ionic compounds, let us use the reaction of silver sulfate and aluminum chloride. Let us assume that the formulas of these two

substances are known to be Ag_2SO_4 and AlCl_3 , respectively, and that the products are known to be aluminum sulfate and silver chloride. All four substances are ionic compounds, but silver chloride is only slightly soluble. We write first, then, an incomplete draft of the equation



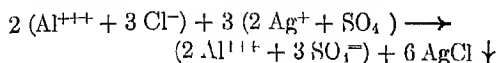
As written, the formulas for aluminum sulfate and silver chloride may not be correct, let us check them before proceeding. The valence numbers of Ag^+ and Cl^- are $+1$ and -1 , the formula of silver chloride is correct as it stands. The valence numbers of aluminum and sulfate ions, however, are not the same. In aluminum sulfate, and in its solution, the relative numbers of Al^{+++} and $\text{SO}_4^{=}$ ions must be such that the total valence number of the aluminum ions is the same as that of the sulfate ions, i.e., the total number of units of positive charge on the aluminum ions must be the same as the total number of units of negative charge on the sulfate ions. This condition is met when there are two aluminum ions for three sulfate ions — $2 \text{Al}^{+++} + 3 \text{SO}_4^{=}$. For solid or undissolved aluminum sulfate, therefore, the formula, as usually written, is $\text{Al}_2(\text{SO}_4)_3$. We may now write the equation as



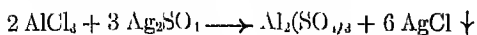
The formula of silver chloride, written as $\text{AgCl} \downarrow$, shows that this substance does not remain in solution, it precipitates as a solid.

The equation is not yet balanced. The fact that three sulfate ions are necessary (on the right-hand side) shows us immediately that the formula of silver sulfate, in which there is only one sulfate ion, must be used (on the left-hand side) three times. Likewise, the formula of aluminum chloride must be used twice in writing the left-hand side of the equation, to supply the two ions of aluminum that are required by the formula of aluminum sulfate on the right-hand side. The equation is now balanced with respect to aluminum and sulfate ions. At the same time that we were balancing the numbers of these ions, we were adding six ions of chlorine and six of silver, which are shown on the right-hand side of the equation as $6 \text{AgCl} \downarrow$, since the valence number of each

of these ions is 1. The balanced equation, therefore, is



This equation is also written in the following form, which shows the formulas of all the substances involved but does not indicate that, in solution, they exist as independent ions



This method of balancing equations can be used for reactions of substances that are not composed of ions as well as for those that are; it cannot be used, of course, for reactions in which there are changes in the valence numbers of some of the elements or ions, and which, therefore, involve oxidation and reduction.

In the reaction that we have just discussed, the aluminum and the sulfate ions are not actually involved, if they are allowed to remain in solution; indeed, our equation shows that they existed as ions before the change occurred, and that they also exist as ions afterward. Of course, if the water in which they are dissolved is removed by evaporation, they will form crystals of aluminum sulfate. In solution, the only change that occurs involves the formation of the precipitate of silver chloride from silver and chloride ions. Some prefer to show only this change in the equation, omitting entirely the other ions that entered the solution with those of silver and chloride



This procedure is acceptable and, indeed, has much to recommend it.

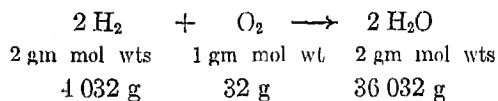
CHEMICAL CALCULATIONS

18. What Information Concerning a Reaction is Given by the Equation?

When we write $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$, the equation states that two gram-molecular weights of hydrogen react with one gram-molecular weight of oxygen to form two gram-molecular weights of water. The formulas used in the equation also show the composition of each substance in terms of the kinds of elements and the number of atoms of each in a molecule, or at least the

relative number of each kind of atom in the compound, since we must remember that some compounds do not consist of molecules. *Most important of all, the equation shows the proportions by weight of the reacting substances and the products.* We use the equation, therefore, when we wish to determine the weight of one substance that will react with, or that can be produced from, a definite weight of another. This is probably the most common type of problem the chemist is called upon to solve.

If, for example, we must find the weight of water that can be produced from 40 g of oxygen, we first write the equation for the reaction



The equation states that 32 g of oxygen produces 36.032 g of water. To determine the weight of water that can be formed from 40 g of oxygen, we may proceed as follows.

32 g of oxygen produces 36.032 g of water

$$1 \text{ g of oxygen produces } \frac{36.032}{32} \text{ g of water}$$

$$40 \text{ g of oxygen produces } 40 \times \frac{36.032}{32} \text{ g of water}$$

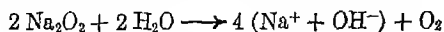
Not only does the equation express the weight relations of the substances involved in the reaction, but it also expresses volume relations for all gaseous substances that take part in the change that it describes. Since gram-molecular weights of gases occupy 22.4 liters under standard conditions, the equation for the reaction between hydrogen and oxygen states that 11.8 liters of water vapor, at 0°C , and 760 mm, are produced from 44.8 liters of hydrogen and 22.4 liters of oxygen.

19. Solutions of Other Problems

In order that the student may become thoroughly familiar with the solution of problems that involve the weights and volumes of substances that the chemist uses or produces in

different processes, further examples are explained below

(1) What weight of oxygen can be produced by treating 10 g of sodium peroxide with water?



Molecular weight of sodium peroxide =

$$(2 \times 23) + (2 \times 16) = 78$$

Molecular weight of oxygen = 32

The equation shows that whatever weight of sodium peroxide is used, the ratio of its weight to the weight of the oxygen produced must be 156/32. Knowing the value of this ratio, it is a very easy matter to find the weight of oxygen which can be produced from 10 g of sodium peroxide, since x (the weight of oxygen) must be in the same ratio to 10 as 32 is to 156

$$156/32 = 10/x$$

$$156x = 320$$

$$x = 2.051 \text{ g}$$

(2) What volume of oxygen at 20° C and 720 mm. can be produced from 10 g of sodium peroxide? The solution of the first problem shows that 2.051 g of oxygen is produced. The volume of this weight of oxygen, under standard conditions, can be calculated since we know that the gram-molecular volume is 22.4 liters. Hence, 32 g of oxygen occupies 22.4 liters. The volume occupied by 2.051 g is in the same ratio to 22.4 liters as 2.051 is to 32

$$2.051/32 = x/22.4$$

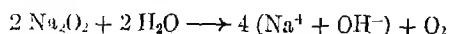
$$32x = 45.94$$

$$x = 1.435 \text{ liters} = 1435 \text{ ml}$$

To find the volume at 20° C and 720 mm, this volume of 1435 ml must be corrected according to Boyle's and Charles's laws (page 93)

$$V_{20^\circ \text{ and } 720 \text{ mm}} = 1435 \times 293/273 \times 760/720 = 1626 \text{ ml}$$

(3) If sufficient water is added to react with 10 g of sodium peroxide and to make 100 ml of solution, what weight of sodium hydroxide will be present in the solution at the end of the reaction? To what concentration of sodium hydroxide, expressed as gram-molecular weights (or formula weights) per liter, does this correspond?



One gram-molecular weight (78 g) of sodium peroxide produces two gram-molecular weights

(80 g approximately) of sodium hydroxide. Hence, whatever weight of sodium peroxide is used, the weight x of sodium hydroxide that is produced must bear the same relation to that weight as 80 bears to 78. From 10 g. of sodium peroxide we can obtain, therefore,

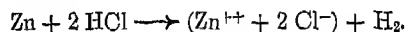
$$78/80 = 10/x$$

$$78x = 800$$

$$x = 10.246 \text{ g of NaOH.}$$

Thus weight of sodium hydroxide is 10.246/40 of one gram-molecular weight. This fraction can also be expressed as 0.256 gram-molecular weight, this figure represents the concentration of sodium hydroxide in 100 ml. A liter of the same solution would contain 102.46 g of sodium hydroxide, or 2.56 gram-molecular (more accurately 2.56 gram-formula) weights (page 140)

(4) What weight of zinc will be required to liberate 2 liters of hydrogen at 10° and 740 mm from a solution containing an excess of hydrochloric acid?



The equation for this reaction states that one gram-atomic weight (65.38 g) of zinc liberates two gram-atomic weights (2.016 g) of hydrogen. The ratio of the weights of hydrogen and zinc must always be equal to 2.016/65.38. In order to use this ratio it is first necessary to find the weight of the volume of hydrogen stated in the problem. Now we know that 2.016 g of hydrogen occupy 22.4 liters under standard conditions, but the two liters mentioned in the problem were measured at 10° and 740 mm. This volume must be converted, therefore, to the correct volume of the same weight of hydrogen at 0° and 760 mm

$$\begin{aligned} \text{Volume (standard)} &= 2 \times 273/283 \times 740/760 \\ &= 1.878 \text{ liters} \end{aligned}$$

Let us say that this volume, 1.878 liters, weighs x grams. Then

$$1.878/x = 22.4/2.016$$

$$22.4x = 3.82$$

$$x = 0.1705 \text{ grams}$$

It is now possible to find the weight of the zinc required to produce 0.1705 g of hydrogen

$$65.38/2.016 = x/0.1705$$

$$2.016x = 11.1473$$

$$x = 5.52 \text{ g of Zn.}$$

THE ENERGY CHANGES DURING REACTIONS

20. Endothermic and Exothermic Reactions

In some chemical changes energy is liberated in the form of heat and light, and in others it is absorbed. In any event, there is usually a noticeable change in the energy content of the substances involved in any reaction. In some instances, the energy liberated or absorbed during the reaction is very important. When we write the equations for these reactions, we must try to show the changes in energy as well as the changes in composition. A reaction that is accompanied by a liberation of energy is said to be *exothermic*. One accompanied by an absorption of energy is *endothermic*. Since the energy that is liberated or absorbed is usually in the form of heat, the energy change during a reaction is usually expressed in calories and is called the *heat of the reaction*. The calorie, it will be remembered, is the quantity of heat required to raise the temperature of one gram of water (at 15°) one degree, Centigrade. This unit of *heat* should not be confused with the degree of *temperature*. The same quantity (number of calories) of heat may be contained in a pint of water and in a gallon, but the temperature of the water in the pint measure would be much higher than the temperature in the gallon. Temperature refers to the intensity factor of heat.

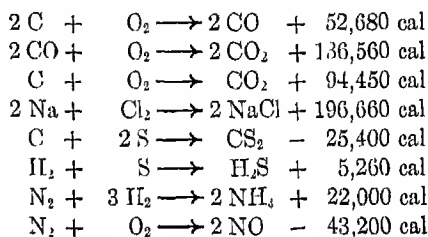
21. Heats of Combustion and Formation

The *heat of combustion* is usually expressed as the number of calories liberated when the gram-molecular weight of the substance burns, although it is sometimes used in speaking of the heat released when one gram of the substance undergoes combustion. The *heat of formation* of a compound is usually expressed as the number of calories liberated or absorbed when one gram-molecular weight of the compound is formed from the constituent elements. This is really the *molar heat of formation*. Thus, the heat of formation of carbon dioxide, as the term is ordi-

narily used, refers to the heat liberated when 44 g. of carbon dioxide is formed by the combination of carbon and oxygen. It does not refer, for example, to the heat that is liberated when carbon monoxide burns to form carbon dioxide.

22. Equations Showing the Heats of Reactions

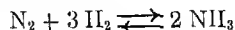
The following examples of endothermic and exothermic reactions will serve to illustrate the differences between the two types of change. The data are for gaseous states of all products except NaCl, which is a solid.



In a way, the heat of formation of a substance is a measure of the stability of the substance. In general, we may say that endothermic compounds are less stable than exothermic compounds.

Review Exercises

1. What weights (in grams) of hydrogen are represented by H and H₂, respectively?
2. Upon the basis of what assumption did Dalton use the formula HO for water? Why do we now assign water the formula H₂O?
3. What does a chemical equation state concerning the reaction that it represents?
4. State all the facts which are expressed by the following equation



5. What information must be available for the determination of the actual formula of a compound? How is this information obtained for gaseous substances?
6. What facts concerning the compounds that they represent are shown by the following formulas? Calcium sulfate, Ca⁺⁺SO₄⁼, ethane, C₂H₆, ammonia, NH₃, potassium nitrate, K⁺NO₃⁻, and sucrose (sugar), C₁₂H₂₂O₁₁.
7. The weight of 1335 ml. of a pure gaseous substance measured at 100° C. and 740 mm. is

- 2 589 g Analysis shows that it consists of 62.07 per cent of carbon, 27.59 per cent of oxygen, and 10.34 per cent of hydrogen. What is the formula of the compound?
- 8 What is the simplest formula of a solid substance which has the following percentage composition? Sodium 32.39 per cent, phosphorus 21.85 per cent, oxygen 45.06 per cent, hydrogen 0.70 per cent
- 9 Calculate the percentage composition of each of the following substances NH_3 , CO_2 , $\text{C}_2\text{H}_6\text{O}$, H_2O , Fe_2O_3
- 10 What volume of oxygen (standard conditions) can be produced by the decomposition of 26 grams of water? What volume of hydrogen is produced at the same time?
- 11 What weight of tin will react with chlorine to form 110 g of stannic chloride in which the valence of tin is 4?
- 12 What volume of carbon dioxide measured at 20° and 760 mm can be produced from 1 kg. of CaCO_3 by the following reaction?
- $$\text{CaCO}_3 (\text{heat}) \longrightarrow \text{CaO} + \text{CO}_2$$
- 13 Propane has the formula C_3H_8 . Write the equation to show the reaction when this substance burns completely. What volume of oxygen (standard conditions) would be required to burn 132 g of propane? Assuming that the temperature of the gases resulting from the reaction is 100°C , how would the volume of gases after the reaction compare with the combined volumes of oxygen and propane in the original mixture, if the temperature of the mixture in the beginning was 0° and the pressure remains constant? What volume of carbon dioxide, under standard conditions, would be produced?
- 14 The formula for silver oxide is Ag_2O . What weight of carbon will be required to produce 20 g of metallic silver from silver oxide by the following reaction?
- $$\text{Ag}_2\text{O} + \text{C} \longrightarrow \text{C'O} + 2\text{Ag}$$
- 15 Define exothermic and endothermic reactions and give examples of each
- 16 How many grams of water could be heated from 0°C to 100°C by the complete utilization of the heat liberated when 10 g of carbon is converted by combustion into carbon dioxide?
- 17 What weight of ten per cent sulfuric acid solution must be used to produce ten standard liters of hydrogen by action upon an excess of zinc? If the specific gravity (weight per ml) of this solution is 1.072, what volume of sulfuric acid would be required?
- 18 Hydrogen is passed over 50 g. of heated magnetic oxide of iron (Fe_3O_4). The water which forms as a result of the reaction weighs 12 g. Calculate (a) the weight of the solid residue after the reaction, and (b) the volume of hydrogen (under standard conditions) that reacted
- 19 What are the valences of the elements combined with oxygen in the following oxides? Bi_2O_3 , PbO , PbO_2 , B_2O_3 , P_2O_5 , SiO_2 , Ag_2O . Write the formulas for the corresponding chlorides
- 20 Using the information on pages 143-44, write the formulas for calcium arsenate, barium phosphate, aluminum acetate, ammonium carbonate, and magnesium chromate
- 21 Name the following compounds CaSO_4 , $(\text{NH}_4)_3\text{PO}_4$, $\text{Cu}_3(\text{AsO}_3)_2$, $\text{Ba}_3(\text{AsO}_4)_2$, NH_4NO_3 , $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$
- 22 Which of the following formulas are correct? K_2CO_3 , CuS_2 , Na_2PO_4 , $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$, MgCO_3 , $\text{Al}(\text{OH})_2$
- 23 Complete and balance the following equations
- (a) Barium nitrate + Ammonium chromate \rightarrow
 (Soluble) (Soluble)
 Barium chromate + Ammonium nitrate
 (Insoluble) (Soluble)
- (b) Ammonium phosphate + Calcium chloride \rightarrow
 (Soluble) (Soluble)
 Calcium phosphate + Ammonium chloride
 (Insoluble) (Soluble)
- (c) Magnesium arsenite + Cupric sulfate \rightarrow
 (Soluble) (Soluble)
 Cupric arsenite + Magnesium sulfate
 (Insoluble) (Soluble)
24. A compound contains 1.8 g of carbon, 0.3 g of hydrogen, and 0.8 g of oxygen in a sample weighing 2.9 g. If one liter of this compound in its gaseous state weighs 2.5893 g (volume measured under standard conditions), what is the molecular formula of the compound?

Reference for Further Reading

Chapin, W. H., and L. E. Steiner, *Second Year College Chemistry*. 4th ed., New York: John Wiley and Sons, 1938

GENERAL CLASSIFICATION OF COMPOUNDS

*I am fully aware that names are one thing,
and science another*

FARADAY

1. Introduction

In a previous chapter we have seen that substances may be classified as elements and compounds. So far, we have studied two elements, oxygen and hydrogen, at some length, and we have learned a few isolated facts concerning several other elements and a few compounds. It is evident that a continuation of this method of studying each element and its compounds as individual substances would lead in time to the collection of a vast amount of unorganized information instead of classified and organized knowledge of the kind that the study of chemistry, as a science, should reveal to the student.

Before considering other elements and their compounds, let us turn our attention, therefore, to substances in general with the view of learning the classes into which they can be divided and the characteristic and distinguishing properties that belong to each class. Instead of attempting to learn the detailed behavior of each and every substance, it is often sufficient to associate a substance with the class to which it belongs. Hydrochloric acid, for example, possesses few properties that are peculiar to itself; in general, its properties are those of all acids.

The elements themselves fall into definite classes, usually called families, all the ele-

ments of a family form compounds that have similar properties, formulas, and structures. The classification of the elements is discussed in Chapter 15, page 218. At this time, we are concerned with classes of compounds.

2 Compounds Classified upon the Basis of Structure

In Chapter 4 we classified compounds as *ionic* and as *covalent or molecular*. These two types of compounds differ considerably in their properties. The ions of ionic compounds possess electrical charges which cause the ions to be held together rather firmly. The molecules of covalent compounds are not electrically charged, and therefore the forces that bind them together in a body of such a substance are relatively weak. We find, generally speaking, that ions are not easily separated, hence ionic compounds have relatively high melting and boiling points. Their liquid states are excellent conductors of electricity. Covalent compounds, on the other hand, have relatively low melting and boiling points. Many of them, under ordinary conditions, are gases. They are non-conductors of electricity in their liquid state.

Covalent substances may be still further classified as *polar* and *non-polar*. The molecules of polar substances act as *dipoles*.

Let us explain by using a few examples of such substances. In the molecule of hydrogen chloride,



chlorine has a much stronger attraction for electrons than hydrogen has, and, although the chlorine atom does not remove an electron completely from the atom of hydrogen, we may reasonably assume that the pair of electrons spend much more time in rotating around the nucleus of chlorine than around the hydrogen nucleus. We may represent this condition in our formula by placing the electron pair that binds these two atoms together nearer chlorine. It now becomes apparent that the negative charges (electrons) are located on one end of the molecule, and that the other end is a more or less independent proton (positive charge). We may consider the molecule, therefore, as a particle having two poles, one positive and one negative.

In the water molecule, the two atoms of hydrogen are not arranged symmetrically on opposite sides of the oxygen atom, instead, they are 105° apart (Figure 75). In this

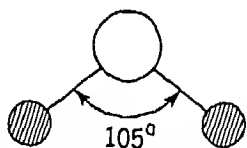


Figure 75 The Water Dipole
The two atoms of hydrogen are 105° apart

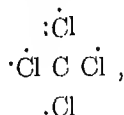
molecule, the center of all the electrons is the center of the oxygen atom, but the center of distribution of the protons is not at the same point. Hence this molecule is also a dipole.

The molecules of a free element are non-polar. In the molecules of hydrogen and chlorine, for example,



the pairs of electrons unite atoms of the same element. Since the atoms that it joins have

exactly the same attraction for electrons, a pair is located midway between the two atoms; and hence the centers of distribution of electrons and protons coincide. There are no poles of a molecule that has a symmetrical structure of this kind. Similarly, in the molecule of carbon tetrachloride,



the electrons and protons of the four chlorine atoms are arranged symmetrically around the carbon atom instead of having their centers of distribution at different points. Hence carbon tetrachloride is a non-polar compound.

The molecules of polar substances exert considerable attractive influences upon one another. The positive pole of one molecule attracts the negative pole of another. As non-polar molecules cannot act in this manner, they are much more nearly independent of one another. In general, therefore, polar substances are found to have higher boiling and melting points than non-polar substances. Then liquid states, however, are not conductors of the current of electricity because they do not contain separate positive and negative particles.

3 Electrolytes and Non-Electrolytes

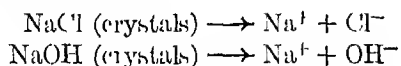
One useful basis of classifying compounds depends upon the fact that some compounds, when dissolved in water or certain other solvents, conduct the current of electricity, some of these compounds are also conductors in their pure, liquid states; thus, both a solution of sodium chloride in water and melted sodium chloride are conductors. When these substances or their solutions act as a part of a circuit in which there is an electric lamp, for example, the lamp will "light," just as if the entire circuit were made of copper wire. It is true that solutions, like wires, vary greatly in their ability to conduct the current, but we are speaking here of a solution

that conducts at least moderately well. Hydrochloric acid (HCl) sodium hydroxide (NaOH), and sodium chloride (NaCl) are examples of substances that form solutions of high conductivity. Because of their ability to conduct the current, they are called *electrolytes*. Glycerine, sugar, and naphthalene (moth balls) are examples of non-conductors or *non-electrolytes*. We believe that the ability of solutions of acids, bases, and salts to conduct the electric current depends upon the presence of *ions* in these solutions. An ion is an electrically charged atom or group of atoms (radical).

4 How Ions are Produced in Solutions of Electrolytes

Many of the substances that produce ions in solutions are substances, like sodium chloride, that have been produced by the transfer of electrons from one element to another, e.g., from sodium to chlorine. Sodium hydroxide, as we have seen, is also a substance of this kind. These substances are composed of ions in the crystal state, and when the crystals are dissolved, the ions are set free from the fixed positions that they occupy relative to one another in the crystal.

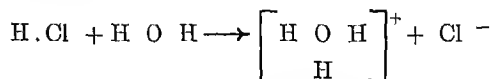
We may represent this condition by the following equations.



Many compounds of hydrogen with non-metallic elements (HCl, for example) or with radicals (H₂SO₄, for example) also form aqueous solutions that are conductors, we must conclude, therefore, that their solutions contain ions. These substances do not appear to be composed of ions before they are dissolved, for example, hydrogen chloride (HCl) in the pure, liquid form is not a conductor. The ions that make their solutions conductors must be formed, then, when the compounds dissolve in water.

By what reactions are these ions produced? The oxygen atom of the water molecule has eight electrons in its outermost group; four

of these it shares with two atoms of hydrogen. The other pairs are unused. By means of one of these free pairs, the oxygen atom of the water molecule might, under favorable conditions, form a co-ordinate covalent bond with a proton, which has no electrons, and which, therefore, can share a pair belonging to oxygen. In hydrogen chloride the chlorine atom and the hydrogen atom share two electrons. Now when hydrogen chloride dissolves in water, the following reaction may occur:

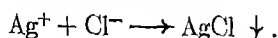


When the hydrogen atom is separated from the chlorine atom, it leaves its electron with the latter, which thus becomes a negatively charged ion, Cl⁻. When the positively charged hydrogen ion (really a proton) attaches itself to the oxygen atom of the water molecule, it forms a positive ion, H₃O⁺, called the *hydronium ion*.

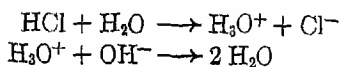
There is some evidence to indicate that more than one molecule of water may combine with the hydrogen ion, or proton, and the formula of the ion is sometimes written as H(H₂O)_n⁺, the subscript *n* represents the number of water molecules for each hydrogen ion. This ion may be regarded as a *hydrated hydrogen ion*. A hydrate is a compound (or ion, in this instance) in which one or more molecules of water are combined with a molecule, or ion, of another substance. Whenever we have occasion to refer to the ions that exist in a solution of an acid, we shall indicate the ion involving the hydrogen that the acid releases as H₃O⁺ (or H⁺·H₂O) or simply as H⁺. We are justified in using H⁺, since the water molecule is a more or less inert partner of the H⁺ in H₃O⁺. In a reaction, for example, it is the H⁺ of the H₃O⁺ ion that combines with another ion or radical, and the H₂O molecule is again set free. We shall later return to this subject when compounds of this nature are discussed in another chapter. Many ions form hydrates similar to the hydronium ion.

5. The Reactions of Electrolytes

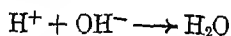
In general, the three classes of compounds that produce ions in aqueous solutions are *acids*, *bases*, and *salts*. Acids are represented in our present discussion by HCl; bases by NaOH; and salts by NaCl. The ions liberated when these substances are dissolved may combine with other ions that may be present to produce new compounds. Thus, the chloride ion from sodium chloride and the silver ion from silver nitrate form slightly soluble silver chloride when they are placed in the same solution



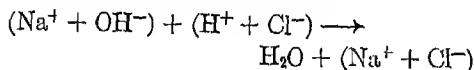
Similarly, the hydrogen ions of an acid and the hydroxyl ions of a base combine in solution to form molecules of water. The acid and the base are said to *neutralize* each other. Using HCl as the acid, the equations are



Or representing H_3O^+ simply by H^+ , as we have agreed to do



The complete reaction between NaOH and HCl may be written as follows



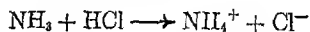
6. Acids, Bases, and Salts

An acid may be defined as a substance that liberates hydrogen ions (protons, page 49) for reactions with other substances. In aqueous solutions, acids form ions when they react with molecules of water to form hydronium ions, H_3O^+ . When the acid reacts in solutions with another substance, it is this ion that supplies H^+ for the reaction.

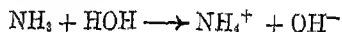
Bases are substances that combine with the H^+ ion supplied by acids or by the hydronium ion H_3O^+ of acids in aqueous solution. The most familiar base is the hydroxyl ion, OH^- , which reacts with the hydrogen ion, or with H_3O^+ , to form water. For this

reason, a base is sometimes defined as a substance (NaOH, for example) that liberates hydroxyl ions when dissolved in water. Since the hydroxyl ion is not the only kind of particle that combines with H^+ , our use of the term base must be expanded somewhat to include all substances, composed of either molecules or ions, that will accept the protons that an acid can supply.

When water reacts with hydrogen chloride to form hydronium ions and chloride ions, it accepts the protons (H^+) from molecules of HCl, and therefore acts as a base. When ammonia, NH_3 , reacts with hydrogen chloride, ammonia is the base



When water reacts with ammonia, the protons are supplied by molecules of water, which therefore acts as an acid



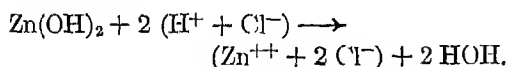
Although ammonia, water, and hydrogen chloride are not, in their pure states, composed of ions, they produce ions when they react as acids or bases. Our previous statement — namely, that substances capable of producing ions in solutions are salts, acids, and bases — is still correct, although we must note that *not all* acids and bases are composed of ions in their pure states, and that they do not always produce ions when they react. The essential feature of a reaction between an acid and a base is that one or more protons are transferred from the acid to the base. If the base is an ion, such as OH^- , its acceptance of a proton may result in the formation of a neutral molecule, such as water, if the base is a molecule, such as HOH, its acceptance of a proton produces an ion, such as H_3O^+ .

7. Hydroxides

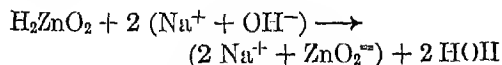
In the preceding section we have stated that the hydroxides of metals, such as NaOH, supply hydroxyl ions and that, because they do so, they are sometimes referred to as bases, although it is the hydroxyl ion that is the real base. We may also speak of the hydroxides of non-metallic elements, but this practice is not in keeping with the usual terminology. Instead of referring to a

certain compound of chlorine, hydrogen, and oxygen as chlorine hydroxide, ClOH , we call it hypochlorous acid and write its formula as HClO . This formula emphasizes the fact that, when this substance reacts with others which can accept protons, it gives up its hydrogen ion, or proton, leaving the hypochlorite ion, ClO^- , it does not produce Cl^+ and OH^- ions. Similarly, we might consider the three acids H_2SO_3 , H_3PO_3 , and H_4SiO_4 as hydroxides and assign them the formulas $\text{SO}_2(\text{OH})_2$, $\text{P}(\text{OH})_3$, and $\text{Si}(\text{OH})_4$. The first formulas, however, are more in agreement with the behavior of these compounds; they react with bases to supply hydrogen ions, or protons, but not with acids to supply hydroxyl ions or to accept protons.

The real distinction, therefore, between different compounds containing hydroxyl groups, the factor that determines whether they react as bases or as acids is the kind of ions that they produce. The hydroxides that act as bases in aqueous solutions form hydroxyl ions, and those that act as acids produce hydrogen ions. Some hydroxides are capable of functioning as an acid under certain conditions and as a base under others, they can and do produce both hydrogen and hydroxyl ions. Zinc hydroxide, $\text{Zn}(\text{OH})_2$, reacts in the same way as any other hydroxide of a metal with an acid, such as hydrochloric acid:



It also reacts with sodium hydroxide as an acid

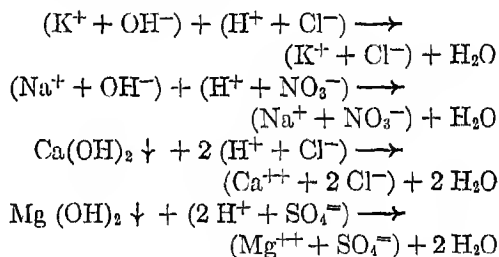


Hydroxides that can act both as an acid and a base are classified as *amphoteric*, or, in more recent chemical literature, as *amphiprotic*, hydroxides. Other amphoteric hydroxides are those of aluminum, chromium, lead, and tin.

8. Salts

Salts are compounds composed of posi-

tively charged ions (usually metallic ions) and negatively charged ions of an acid. In some salts formed from bases like NH_3 , or NH_4^+OH^- , the positive ion may be a radical, e.g., the ammonium ion, NH_4^+ , in ammonium chloride. Salts are produced by several kinds of reactions but most frequently by reactions between acids and the hydroxides of metals. When a solution containing HCl is mixed with one containing NaOH , sodium and chloride ions remain in the solution after the hydroxide and hydrogen ions are converted into molecules of water. If the water is evaporated, these ions form crystals of the salt. The simplest salts are composed of a metal and a non-metal, e.g., NaCl . Others are composed of a metal and a radical, e.g., Na_2SO_4 , KClO_3 . In every salt the particles (atoms and radicals) that make up the salt are ions



The salts formed in these reactions are potassium chloride, KCl , sodium nitrate, NaNO_3 , calcium chloride, CaCl_2 , and magnesium sulfate, MgSO_4 .

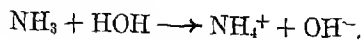
9. Properties of Acids

Lemons, oranges, and grapefruit contain citric acid, sour milk contains lactic acid, and vinegar is a solution of acetic acid. As our acquaintance with these substances indicates, acids are characterized by a sour taste. They have other common properties. In aqueous solutions they produce definite changes in the colors of certain substances called *indicators*. For example, they change blue litmus to red, and they make a red solution of phenolphthalein colorless, if added in excess of the quantity required to react with any base that may be present. They react

with the hydroxides of metals and with ammonium hydroxide and similar hydroxides, to form salts and water, with such bases as ammonia, NH_3 , they form only salts, e.g., NH_4^+Cl^- . All acids supply hydrogen ions, or protons, when they react with bases, and their many common properties depend upon this characteristic behavior. In aqueous solutions they react with water molecules, but not all to the same extent, to form hydronium ions, which are responsible for the acidic properties of these solutions, the real acid that reacts with bases in such solutions, therefore, is this ion, H_3O^+ . The most frequently used acids in the laboratory are hydrochloric, HCl ; nitric, HNO_3 ; sulfuric, H_2SO_4 , and acetic, $\text{HC}_2\text{H}_3\text{O}_2$.

10. Properties of Bases

Solutions of hydroxide-bases, such as NaOH , are bitter in taste. They also produce definite color changes in solutions of indicators; they change red litmus to blue and colorless phenolphthalein to red. They supply hydroxyl ions to react with hydrogen ions of acids to form water and with other ions to form other hydroxides; for example, a precipitate of slightly soluble cupric hydroxide, $\text{Cu}(\text{OH})_2$, is formed in a solution to which sodium hydroxide and cupric chloride are added. The most frequently used hydroxide-bases in the laboratory are sodium hydroxide, NaOH , potassium hydroxide, KOH , calcium hydroxide, $\text{Ca}(\text{OH})_2$; and ammonia, which may react directly as a base (see above), or which forms with water a solution containing ammonium hydroxide, NH_4^+ and OH^- ions



Solutions of these substances are frequently described as *alkaline*.

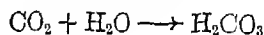
11. Oxides

The group of oxides includes many substances that have very diverse physical appearances. The list includes, for example, such diverse substances as carbon dioxide,

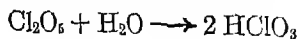
which is exhaled from the lungs and which is present in the gases that escape from burning wood or coal, the oxide of iron, Fe_2O_3 , which we know as iron rust, the black oxide of copper, CuO ; quicklime, CaO , and silica, SiO_2 , which we know best as sand or quartz. Many of the oxides of non-metals are gases (CO_2 , SO_2 , and NO), but those of the metals are solids. Hence the oxides as a class possess few physical properties in common. Chemically, they also differ widely, and to find common properties that allow us to discuss them as groups of related substances we must further classify them as oxides (1) of non-metals and (2) of metals.

12. Oxides of Non-Metals

The oxides of the non-metallic elements that react with water form acids (page 70) and are called acidic oxides.



This is not a general method of producing acids, since there are several acids (HCl , HBr , HI , etc.) that contain no oxygen. The composition of each of the inorganic acids that contain oxygen, however, can be represented in terms of the combining proportions of water and the oxide of some non-metal. Thus, chloric acid, HClO_3 , may be regarded as formed from one molecule of water and one molecule of the oxide, Cl_2O_5 .

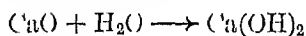


Oxides that react with water to form acids, or that may be formed by the removal of water from acids, are called *acid anhydrides*. The student is advised to determine the anhydrides of the following acids: nitric, HNO_3 , nitrous, HNO_2 , sulfurous, H_2SO_3 , sulfuric, H_2SO_4 , phosphorous, H_3PO_3 , phosphoric, H_3PO_4 , hypochlorous, HClO ; arsenic, H_3AsO_4 , carbonic, H_2CO_3 , boric, H_3BO_3 ; iodic, HIO_3 ; and silicic, H_2SiO_3 .

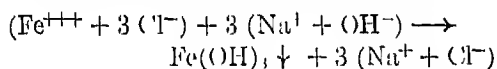
13. Oxides of the Metals

The oxides of the metallic elements react with water to form hydroxides, which, if

soluble in water, give solutions containing the hydroxyl ion and are therefore said to act as bases. The oxides of sodium, potassium, calcium, strontium, and barium react very readily with water. The reaction of calcium oxide (CaO), which we call "quicklime," with water is very vigorous. When water is poured upon lumps of lime, large quantities of heat are evolved, and this heat changes some of the water into steam. The lumps of lime swell and then crumble to a fine, white powder consisting of "slaked" lime (calcium hydroxide).



Some of the oxides react very slowly with water — the oxides of magnesium and silver, for example. Others do not appear to react at all. Hence, as in the case of oxygen-acids, reaction with water is not a general method for the preparation of all hydroxides. An indirect method of preparation is often used. If we wish to prepare a sample of ferrie hydroxide, for example, the following reaction is easier to employ and produces a much more definite product.



Since ferrie hydroxide is slightly soluble, it is easily separated by filtration from the sodium chloride, which remains in solution.

14. Hydrus Oxides

The hydroxides of many of the metals are only slightly soluble. When they are produced, as shown above for ferrie hydroxide, Fe(OH)_3 , the substance that precipitates is not always the same. Because of this variation in composition and because, in writing equations, it is much more convenient to represent the precipitated substance as a normal hydroxide, e.g., Fe(OH)_3 , the actual composition is usually not indicated. Actually, the gelatinous precipitates that are produced when a soluble hydroxide, such as NaOH , is added to a solution of a salt of a metal, such as FeCl_3 , are *hydrus oxides* to

which, in the case of iron, we might assign the formula, $\text{Fe}_2\text{O}_3 (\text{H}_2\text{O})_n$, in which n has different small integral values depending upon the conditions under which the compound is produced. The formula $\text{Fe}_2\text{O}_3 (\text{H}_2\text{O})_3$ would correspond, of course, to the normal hydroxide, 2Fe(OH)_3 . Other metals that form hydrus oxides are lead, aluminum, chromium, and tin.

15. The Structure of Oxides

The oxides of the metallic elements are ionic compounds, in their solid states their structures are crystalline patterns of ions. Calcium and magnesium oxides, for example, form crystals in which ions of the metals and of oxygen, $\text{O}^{=}$, are arranged in a definite pattern, called a crystal lattice. Figure 76 shows the lattice of calcium oxide.

The oxides of the non-metallic elements are covalent compounds and therefore are composed of molecules. In their solid states these compounds also form crystals, but the particles of which their structures are composed are molecules instead of ions.

16. The Names of Oxides

The naming of the oxide of an element that combines with oxygen in a single proportion is a simple matter. Thus, we speak of calcium oxide, magnesium oxide, and so on. But some elements form two, three, four, or even five oxides, clearly, the several oxides of an element cannot all be called by the same name. In different oxides, of course,

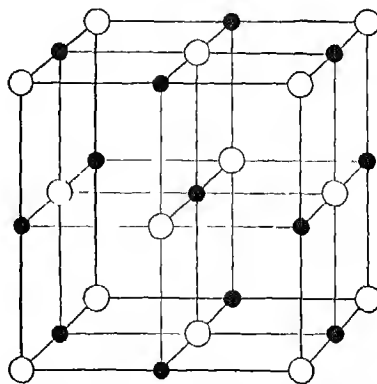


Figure 76 Crystal Structure of Calcium Oxide
Shaded Circles Represent Atoms of Oxygen

the metal displays different valence numbers. If an element forms only two oxides, the names assigned to the two compounds may differ only in the ending affixed to the name of the element. The ending *-ous* is used to denote the lower valence and the ending *-ic* to denote the higher. Thus, we have two oxides of mercury, copper, iron, and tin

Hg ₂ O, mercurous oxide	FeO, ferrous oxide
HgO, mercuric oxide	Fe ₂ O ₃ , ferric oxide
Cu ₂ O, cuprous oxide	SnO, stannous oxide
CuO, cupric oxide	SnO ₂ , stannic oxide

This system of terminology is applied to the oxides of several metals. Most of the oxides of the non-metals and those of all elements that form several oxides are named in a different manner. Very often the name indicates the number of oxygen atoms in a molecule

CO, carbon monoxide	P ₂ O ₄ , phosphorus tetroxide
CO ₂ , carbon dioxide	N ₂ O ₅ , nitrogen pentoxide
Bi ₂ O ₃ , bismuth trioxide	PbO ₂ , lead dioxide

17. The Names of Acids and Hydroxide-Bases

Acids that contain the same elements — H₂SO₃ and H₂SO₄, for example — must have different names. If there are only two such acids of a non-metallic element, the endings *-ous* and *-ic* are used as in the naming of some oxides. The former is used to designate the acid in which the non-metallic element has its lower valence number, thus, for the two acids of sulfur, H₂SO₃ is *sulfurous*, and H₂SO₄ is *sulfuric acid*. The anhydrides of these two acids are sulfur dioxide, SO₂, and sulfur trioxide, SO₃, the valence numbers of sulfur in the two compounds are 4 and 6, respectively.

If there are more than two oxygen-acids of the same element, they cannot be distinguished by the use of two suffixes. Thus, there are four oxygen-acids of chlorine, HClO, HClO₂, HClO₃, and HClO₄. Their anhydrides are Cl₂O, Cl₂O₃, Cl₂O₅, and Cl₂O₇, respectively. The names *chlorous* and *chloric* are assigned to the second and third acids, respectively. The first, HClO, shows a

smaller combining capacity of chlorine than chlorous acid, HClO₂. It is also called chlorous acid, but the prefix *hypo* is added to distinguish it from HClO₂. The fourth acid represents the highest combining capacity of chlorine. The prefix *per-* is added to distinguish this acid from HClO₃.

Acids which contain only two elements are called binary acids and are named by attaching the prefix *hydro-* and the suffix *-ic* to the name of the element combined with hydrogen. The name is sometimes shortened, as in *hydrochloric acid*. Other binary acids are hydrosulfuric, H₂S, hydrobromic, HBr, and hydriodic, HI. The names and formulas of the five acids of chlorine are listed below.

HCl	hydrochloric acid
HClO	hypochlorous acid
HClO ₂	chlorous acid
HClO ₃	chloric acid
HClO ₄	perchloric acid

If a given metal forms two hydroxides, the suffixes *-ous* and *-ic* are added to a shortened form of the name of the element. Thus, Fe(OH)₂ and Fe(OH)₃ are called ferrous and ferric hydroxide, respectively.

18. The Names of Salts

The names of salts that contain only two elements consist of two parts. (1) the name of the metal from whose hydroxide the salt is prepared, or the name of the positive radical, such as NH₄⁺, and (2) the name of a non-metallic element (the name is usually shortened) to which the suffix *-ide* is attached. If the second portion of the salt is a radical (as in MgSO₄, NaNO₃, etc.), the second word is the name of this radical. The names of these radicals usually end in *-ate*. Thus, CaCO₃ is calcium carbonate, MgSO₄ is magnesium sulfate, KClO₃ is potassium chlorate, and so on. But if there are two or more radicals, showing different combining capacities of the same non-metal with oxygen, different endings and prefixes must be employed, as in the naming of acids. The salts corresponding to the *-ous* acids are given

names ending in *-ite*. Those that correspond to the *-ic* acids are distinguished by the suffix *-ate*. For the "hypo—ous" acids the corresponding salts are the "hypo—ites". The "per—ic" acids form salts which are named the "per—ates". Thus the four sodium salts of the oxygen-acids of chlorine are

NaClO , sodium hypochlorite

NaClO_2 , sodium chlorite

NaClO_3 , sodium chlorate

NaClO_4 , sodium perchlorate

The sodium salts of sulfurous and sulfuric acids are

Na_2SO_3 , sodium sulfite

Na_2SO_4 , sodium sulfate

Most metals form only one or two salts with chlorine, bromine, iodine, sulfur, and other non-metals. Hence, the endings *-ous* and *-ic* suffice to distinguish between two binary salts of the same elements. CuCl and CuCl_2 are cuprous and cupric chlorides, HgCl and HgCl_2 are mercurous and mercuric chlorides, and FeCl_2 and FeCl_3 are ferrous and ferric chlorides, respectively.

19 Classes of Salts

Salts are very numerous. In fact, they constitute one of the largest classes of substances. They may be classified either upon the basis of the metals from which they are formed, or by groups containing the same radical or non-metal. Thus, we may consider them as groups of sodium salts, calcium salts, non salts, and so on, or we may classify them as chlorides, nitrates, etc., of different metals. Each group shows certain properties common to all its members. For example, all sodium salts impart a yellow color to a flame, and they react in other ways that are characteristic of the sodium rather than of the entire salt. Similarly, all nitrates have certain common properties, such as solubility in water.

20. Inorganic and Organic Compounds

All the salts, all the bases, and all the acids except acetic that have been men-

tioned in this chapter are classified as *inorganic* compounds, because they are associated with inanimate materials. Many of them are produced from ores, rocks, and minerals, such as salt, sulfur, limestone, quartz, and the ores of iron, copper, and other metals, the oxygen and nitrogen of the air and, sometimes, water enter into the formation of some of them. Most *organic* compounds, on the other hand, are related directly or indirectly to living materials — plants or animals. Many organic substances are obtained directly from plant and animal sources: sugar from beets and cane, quinine from the bark of one tree, and rubber from the sap of another, fats from animals and from corn, coconut, and olives, and musk from the musk ox. Many others, however, are only indirectly related to forms of life, some of these are produced by the destructive distillation (heating in the absence of air) of coal, wood, and other like materials. Still others are obtained directly from petroleum which, like coal, is a product — according to the most generally accepted theory of its formation — of changes in the remains of once living matter. But most of the compounds now known to organic chemistry are synthesized, sometimes by many consecutive reactions, from the relatively simple materials obtained from coal, petroleum, and similar sources, and from still simpler substances such as water, hydrogen, oxygen, chlorine, nitrogen, and sulfur. Many compounds thus produced do not exist in plants or animals, and they are not found among the products of their decay. Thus, nitroglycerine does not occur in any living material or in any product of natural origin. It is produced by the action of nitric acid — which may be produced from nitrogen, oxygen, and water — upon glycerine obtained from vegetable and animal fats. Nitroglycerine may therefore be classified as an organic compound. Not all organic compounds are related even as closely as nitroglycerine to organic materials, living or dead; some of them can be built up, at least in part, from almost purely

inorganic substances such as the nitrogen of the air, water, limestone, and coal or coke.

Nevertheless, we have always been dependent, directly or indirectly, upon organisms for most organic compounds. To be sure, we have synthesized many natural products. Wohler was the first to accomplish such a synthesis. In 1828, he synthesized urea ($\text{CO}(\text{NH}_2)_2$). Previously, this substance had been known only as a product of the decomposition of nitrogenous substances in the bodies of animals and had been prepared from the liquid excrement of animals. Since 1828, many naturally occurring substances have been made in the laboratory. We have produced dyes (indigo, for example), perfumes, medicines, flavors, and many other types of substances which are chemically identical with substances found in organic nature. Indeed, we have gone much farther. We have synthesized perfumes more fragrant, medicines more powerful and effective, dyes more brilliant in color, and flavors at least as tasteful as any of those which nature produces. We are no longer dependent upon wood for methyl (wood) alcohol, for it can now be synthesized from carbon monoxide and hydrogen. Many other syntheses of important products might be mentioned. Nevertheless, it is difficult to get away from organic material as the starting point of such syntheses. Even the carbon monoxide used in the synthesis of methyl alcohol is produced by the partial combustion of the carbon in coal or coke. Although we no longer depend entirely upon the rubber tree for our supply of rubber, the artificial product now manufactured to take its place contains in its molecules atoms of carbon that probably were once parts of living forms of matter.

This brings us to the importance of carbon in organic compounds, for this element is present in all of them, organic compounds usually contain hydrogen also, many of them contain oxygen as well, and some contain other elements, such as nitrogen, sulfur, chlorine, bromine, iodine, and even

metals. Only carbon, however, is common to them all, hence, organic chemistry is sometimes defined as the chemistry of the compounds of carbon.

There are more compounds of carbon than of all the other elements combined. Already more than 300,000 have been prepared, and there appears to be no limit to the possible number. Although the number is exceedingly great, most of these compounds can be classified in a relatively few groups. Some of the more important groups are acids, alcohols, ethers, carbohydrates, hydrocarbons, proteins, esters, aldehydes, and ketones. Each group consists of compounds whose molecules are somewhat similarly constituted or contain, at least, a common radical or group of atoms. The members of a class possess many properties in common, and they react with the same types of compounds and form the same kinds of products. The alcohols, for example, react with acids to form esters.

Other Classes of Compounds

By no means all compounds fit into the abbreviated classification offered in this chapter. There is no group to which water can be said to belong. Its formula is written, sometimes, as HOH , since it often reacts by first dissociating into H^+ and OH^- ions. For this reason it is both an acid and a base, but unlike ordinary acids and bases it always supplies one hydrogen ion for each hydroxyl ion. It is, therefore, just as strong an acid as it is a base, but no stronger. Many other compounds, particularly compounds of the non-metals, are members of none of the groups which we have mentioned. Thus, carbon tetrachloride (CCl_4), carbon disulfide (CS_2), phosphorus trichloride and pentachloride (PCl_3 and PCl_5), sulfur chloride (S_2Cl_2), and many other compounds of a similar character cannot be classified as salts, although their formulas may indicate some relationship. The chlorides of metals (true salts) are solids which generally show very little tendency to evaporate at ordinary temperatures. With a few exceptions, they are more soluble in water than in any other liquid, such as alcohol or carbon tetrachloride. In the pure fused state and in aqueous solutions they are conductors of the electrical current. The sulfides of the metals, although not very soluble as a rule, possess approximately the same characteristics as the

chlorides and display in general the typical behavior of salts. The sulfides of the non-metals (carbon disulfide, for example) are generally liquids or gases at ordinary temperatures, are as a rule more miscible with organic liquids than with water, and are non-conductors. The same is true of the chlorides of the non-metals. Carbon tetrachloride, for example, resembles carbon disulfide and is entirely different in appearance, properties, and behavior from sodium chloride. The salts of the metals -- NaCl , for example -- are composed of ions, while the corresponding compounds of the non-metals -- CCl_4 , for example -- are composed of atoms that share electrons.

Review Exercises

1. Define *electrolyte*. What classes of compounds act as electrolytes in solution?
2. Name three compounds that are not electrolytes.
3. What is an ion? How are ions produced in solutions of NaCl and NaOH ?
4. How are ions produced in aqueous solutions of substances such as HCl ?
5. What change occurs when an aqueous solution containing NaOH and HCl are mixed?
6. What properties do acids have in common?
7. What properties do aqueous solutions of the hydroxide-bases have in common?
8. How are salts produced from acids and hydroxide-bases?
9. Define, according to the information now before us, the following: acid, base, salt.
10. Into what two classes are oxides divided upon the basis of their reaction with water?
11. Define acid and basic anhydrides.
12. What are the anhydrides of H_3BO_3 , H_3AsO_4 , $\text{Al}(\text{OH})_3$, H_3PO_4 , H_2CO_3 , and $\text{Mn}(\text{OH})_2$?
13. How are acids which contain two elements named? Illustrate.
14. How are acids that contain three elements (one of which is oxygen and one hydrogen) named? Illustrate.
15. Name $\text{Mn}(\text{OH})_2$ and $\text{Mn}(\text{OH})_3$, FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$.
16. Name Na_2CO_3 , NaNO_3 , NaClO_3 , MgSO_4 , Na_3PO_4 , Na_2S , NaBi , Na_2SO_3 , and Na_2SO_4 .
17. Name the four sodium salts of the four acids composed of hydrogen, chlorine, and oxygen.
18. What are some of the important sources of organic compounds?
19. What acids and what hydroxide-bases must react to form the following salts? K_3PO_4 , CuSO_4 , NH_4NO_3 , CaCO_3 .
20. What difference in chemical behavior justifies the formula of HClO for this compound of chlorine and KOH for the corresponding compound of potassium?
21. The formula for a certain compound of arsenic is usually written as H_3AsO_3 instead of $\text{As}(\text{OH})_3$. Why should one of these formulas be preferred to the other?
22. What weight of sodium hydroxide is required to neutralize completely 200 g. of hydrogen chloride dissolved in water? Express the required weight of sodium hydroxide as gram-molecular (or formula) weights.
23. Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, is an important constituent of fertilizers. How much ammonia would be required to produce a ton of ammonium sulfate?
24. The anhydride of an acid contains 66.645 per cent of bromine and 33.355 per cent of oxygen. What is the simplest formula of the acid?
25. What weight of silver chloride can be made from the chloride ion available in a solution containing 100 g. of sodium chloride, assuming that an excess of silver ion is available?
26. If 100 g. each of silver ion and chloride ion are placed in the same solution, and if the precipitate of silver chloride that forms is removed by filtration, dried, and weighed, what weight of silver chloride should be obtained? Assume that precipitation is complete.
27. How do polar and non-polar covalent compounds differ in structure and in properties?
28. What is a molecular dipole? Give examples and show why the molecule must be considered as a dipole.

References for Further Reading

- French, S. J., *The Drama of Chemistry*
 Hammett, L. P., *Solutions of Electrolytes*, 2d ed., New York: McGraw-Hill Book Company, 1935
 Acids, Bases, and Salts *J. Chem. Ed.*, **7**, 782 (1930), **12**, 109 (1935)

WATER

Everywhere water is a thing of beauty, gleaming in the dewdrop, singing in the summer rain, shining in the ice-gems till the leaves all seem to turn to living jewels, spreading a golden veil over the setting sun, or a white gauze around the midnight moon

GOUGH

1 Introduction

The study of water, as we are to undertake it in this chapter, is somewhat broader than the subject indicates. We are to study the liquid state, and using water as an example, we shall consider many properties that belong to the liquid state of many other substances. These include such phenomena as evaporation, boiling, and freezing. Our study of water, itself, is concerned, first, with the physical properties, which for this substance are of more than usual importance, next, with problems connected with natural water, water supplies, and purification, and finally, with the chemical behavior of water and the character of certain substances called hydrates.

2. The Importance of Water to Plants and Animals

The first chemical compound which we shall study is certainly the most familiar. Our familiarity with water is due to our dependence upon it. All the tissues of our bodies are bathed in it. Dissolved or suspended in it, are the various substances which aid in one way or another in the digestion of food. These same foods, when digested, must be carried to the various parts of the body in aqueous solutions. Likewise, many waste products are eliminated from the body as water soluble substances. Even the oxygen which we breathe must dissolve

in water before it passes through the tissues of the lungs into the blood. The large amount of water in our bodies — this is about 65 per cent of the body's weight — aids in maintaining the average body-temperature. Water requires a relatively large amount of heat to raise its temperature a few degrees, and for this reason it is able to absorb the excess heat of the body without the occurrence of radical changes in temperature. Water also has a relatively high heat of vaporization. More heat is required to evaporate one gram of water than one gram of many other substances. Hence, the body is cooled by the evaporation of water from the skin.

Plants depend upon water to an even greater extent than animals. The plant receives all of the supply of nutrients that it extracts from the soil in the form of aqueous solutions. In it are dissolved, also, the various products involved in the plant's biological activity. The food which is manufactured in the leaves is transported in solution to the different storage places, roots, fruit, seeds. When a young plant starts to grow, this food is again dissolved and is thus carried to the growing parts of the structure. The plant also uses water in the manufacture of its foods, starch and sugar are synthesized by plants from water and carbon dioxide.

Large bodies of water greatly affect climate. In the summer, islands and lands near large lakes

and the sea are cooled by air that blows across them from the water. A relatively large amount of heat must be removed from the air to raise the temperature of the water a few degrees, as compared with the quantity required to raise the temperature of the same weight of air, rocks, and soil the same number of degrees. As the water becomes warmer in the summer, therefore, the air above it is cooled considerably. In the autumn the water gives up heat to the air. As the water's temperature decreases a few degrees, the quantity of heat absorbed by the air is sufficient to make its temperature considerably higher than the temperature of the air above the nearby land. When this warm air blows over the land, it produces a warmer climate than would otherwise prevail. All these effects depend upon the fact that one gram of water requires a larger quantity of heat to raise its temperature one degree than does one gram of air or most other substances or materials.

The same property of water — the relatively large quantity of heat required to raise the temperature of one gram of water one degree — accounts for its use in hot water heating systems. When the water is heated, it absorbs large quantities of heat. When the hot water reaches the radiators, where it cools, it releases this heat to the air of the room and the rest of the surroundings. Hot water is a good medium for the transportation of heat from the boiler room to the rest of the house.

To these important effects and uses of water we should add (1) the parts played by water and ice in erosion and in the weathering of rocks, both of which are important in remaking and shaping the earth's surface, (2) the use of running or falling water as a source of energy second only in importance to fuels — coal, oil, and gas; and (3) the transportation over seas, lakes, and rivers of the world's commerce.

3. Occurrence of Water

Water is present in almost all natural objects and in almost every part of the earth that man can reach. There is water vapor in the air, and water in rocks and in the soil. In addition to the water which wets many rocks or which is mechanically enclosed in

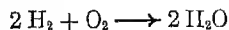
them, some rocks contain it in chemical combination with other substances of which they are composed. This is true, also, of clay. Even objects which appear to be *dry* may show a loss of weight when heated to a temperature which will evaporate the water that they contain without otherwise changing their composition. It is a general rule in the chemical laboratory that a substance, however dry it may appear, must be exposed to conditions (such as a very dry atmosphere) which will remove all water present before the substance can be used in experiments where moisture is undesirable.

Water is present in varying amounts in all food. Green vegetables may contain as much as 90 per cent or even more. Meat, milk, butter, and potatoes contain large percentages of water, and even bread is not "dry."

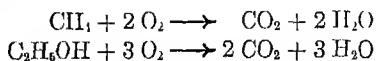
4. The Preparation of Water by Chemical Reactions

Water is so easily obtained that methods of preparing it are unnecessary. It is produced, however, in a number of chemical reactions, most of which are of interest and value not because they produce water, but because they are used to form other substances at the same time.

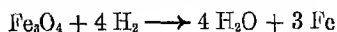
(1) Water can be prepared by burning hydrogen in oxygen (or air) and by exploding a mixture of these two elements



(2) Water is also produced when substances containing hydrogen burn. Examples of such substances are methane (CH_4) and alcohol ($\text{C}_2\text{H}_5\text{OH}$)

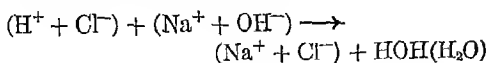


(3) Water is produced when hydrogen reduces oxides or other compounds containing oxygen

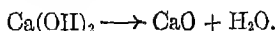


(4) The neutralization of acids and hydroxide-bases results in the formation of salts and water.

The acid supplies hydrogen which reacts with the hydroxyl ion to form water.



(5) Most of the hydroxides of the metals can be decomposed by heating to form the oxide of the metal and water



5. The Composition of Water

Cavendish, in the latter half of the seventeenth century, found that hydrogen (which he called "inflammable air") burned in air to form a liquid. A study of the properties of this liquid showed that it was pure water, but Cavendish did not recognize the complete meaning of his discovery. A few years later, Lavoisier repeated Cavendish's experiments and properly explained them in accordance with his ideas of combustion. He demonstrated that Cavendish's "inflammable air" was an element, which he gave the name hydrogen (page 105), and that the formation of water results when this element combines with Priestley's "dephlogisticated air," which Lavoisier showed to be an element and which he named oxygen (page 64).

A method of determining the proportion by weight of hydrogen and oxygen in water has been described in a previous chapter (page 30). The combining proportions by volume can be determined by using the electric current to decompose water. This method is described on page 110.

PHYSICAL PROPERTIES OF WATER

6. The Physical Properties of Water as a Gas

Water vapor is the stable state of the substance at temperatures above the boiling point. When in the vapor state, water displays the general physical behavior of other gases and obeys the gas laws with certain deviations as in other cases. The discussion of the properties of gases in Chapter 7 ren-

ders unnecessary further treatment of the subject in connection with water.

Water in the gaseous state consists of molecules which are widely separated and which possess little attraction for one another. When the liquid is changed to the gaseous state, energy must be absorbed to overcome the attraction which exists between the molecules and to separate them against the force of this attraction. Due to the absorption of this energy, the gaseous state has a higher energy content than the liquid state of water. This additional energy is liberated, of course, when the substance changes its state in the reverse direction. When one gram of water changes into water vapor at 100° C, the quantity of heat absorbed amounts to 539 calories. This is called the heat of vaporization (per gram).

The gaseous state of water is often called steam. The term steam is also applied to the clouds of condensed moisture that form when water vapor is cooled. In the strict sense, it seems to be desirable to speak of the clouds of condensed moisture as steam and the invisible water in the gaseous state as water vapor. The latter term (vapor) is usually applied to the gaseous state of a substance when it exists as such below its critical temperature.

The student should not think of 100° C, or any other specific temperature, as the temperature at which liquid water changes into the vapor. In an open vessel, the liquid is changing into vapor at all temperatures. Even ice evaporates. The difference between boiling and the slower evaporation that occurs at temperatures below the boiling point will be explained in a later section of this chapter (page 172).

7 The Physical Properties of Water as a Liquid

Pure water is odorless and tasteless. Natural waters often possess taste and sometimes odor because of substances dissolved in them. In thin layers water appears colorless, but in thick layers it has a bluish-green color. It is a very poor conductor of elec-

tricity. At the average pressure of the atmosphere at sea level (760 mm) it boils at 100°C . The boiling point is lower at reduced pressure. At an elevation of 7000 feet, where the pressure of the atmosphere is considerably less than at sea level, the boiling point is 93° , and at an elevation of 30,000 feet it is about 70°C . The freezing point of water is 0°C .

The *density* of water (weight per unit of volume) varies with the temperature. The maximum density is reached at 4°C . Both above and below this temperature the density decreases. This peculiar property is of extremely great importance. Because of it, water freezes from the top downward rather than from the bottom upward. The water in the upper layers is cooled by the air with which it comes in contact. As it is cooled, the density increases and the water sinks. This process continues until the water reaches a temperature of 4°C . As it cools still further, the density decreases, and hence the colder water remains on top where it freezes. When water changes into ice, still further expansion occurs, and the ice, since it is the lighter, floats in the water, this condition also aids in causing water to freeze from the surface downward.

CHANGE IN THE DENSITY OF WATER BETWEEN 0° AND 100°

Temperature	Density g per cc
100	0.958
80	0.972
60	0.983
40	0.992
20	0.998
10	0.9997
4	1.000
0	0.9998

8. Units of Measurement Based upon the Physical Properties of Water

Since water is the most familiar of all liquids, and since it can be obtained readily in the pure state, many common units of

measurements are defined with reference to its properties. Among these the following are important. The unit of heat is the *calorie*. This is the quantity of heat required to raise the temperature of one gram of water one degree ($^{\circ}\text{C}$) at 15° . The *specific heat* of any substance is defined as the quantity of heat (in calories) required to raise the temperature of one gram of the substance one degree. The average specific heat of water is one, although it varies somewhat with the temperature. The *Centigrade scale of temperature* is based upon a zero which is taken as the freezing point of water and a temperature of 100° which is determined as the boiling point (under standard pressure). The Centigrade degree is, therefore, one one-hundredth of the difference in temperature between the freezing and boiling points of water. The weight of a unit-volume (1 cubic centimeter) of water at 4°C has been chosen as the standard density for liquids and solids. The weight of one cubic centimeter of a substance, as compared to the weight of an equal volume of water (usually at 4°C), is called the *specific gravity* of the substance. Thus, the specific gravity of alcohol may be represented as $D_4^{25} = 0.798$. This means that one cubic centimeter of the alcohol under examination weighs 0.798 times as much at 25° as an equal volume of water weighs at 4° .

9. Water as a Solvent

Due to its great abundance and also to the great number of substances that dissolve in it, water is more often employed as a *solvent* than any other liquid. In fact, it is so frequently used as the solvent that a solution is assumed to be aqueous unless some other solvent is specified. Even glass and many other apparently undissolvable substances actually dissolve in water to a slight extent. The solubility of glass in water is pronounced enough to make glass vessels unsuited for the storage of very pure water, this solubility depends, at least to some extent, upon the ability of water to react chemically with

certain substances contained in the glass. The solubility of many substances is increased by reactions between the water and the substances that dissolve.

We sometimes speak of substances as "insoluble" in water. We mean that they are relatively little soluble as compared with other substances which dissolve more readily and in larger quantities. Thus, 6.7 gram-molecular weights of calcium chloride dissolve in 1000 grams of water at 20°, while only 0.00000001 gram-mol weight of silver iodide dissolves in the same quantity of water at the same temperature. Relatively speaking, therefore, calcium chloride is readily soluble, while silver iodide is "insoluble," or more strictly speaking, "very slightly soluble."

10. The Properties of Heavy Water

One gram of heavy water, or *deuterium oxide*, D_2O , can be obtained from about 25,000 grams of ordinary water and sells for about \$1.25 per gram. Salts have slightly different solubilities in H_2O and D_2O , and substances produced by reactions involving the two oxides (such as $NaOH$ and $NaOD$) have some differences. Deuterium oxide has the following physical properties: density, about 1.1, freezing point, 3.8° C, boiling point, 101.4° C, vapor pressure at 100° C., 721 mm. It appears to be toxic to some forms of animals and plants.

11. The Physical Properties of Water as a Solid

At 0° C, under ordinary conditions, water freezes, forming the solid state which we call ice. We cannot say that this is the temperature at which water *begins* to freeze. Under ordinary conditions water does freeze at this temperature, but it is possible to cool water several degrees below 0° before freezing begins. Water which is cooled below 0° without the formation of ice is said to be *undercooled*. This condition results only when water is cooled in the absence of any ice, in a container with smooth walls, and when the liquid is not agitated. If a piece of ice is dropped into undercooled water, freezing begins immediately, and the temperature rises to zero and remains at that point as long as

there is any liquid. Hence, properly speaking, 0° C is the temperature of a water-ice mixture. If heat is added to the mixture, the ice melts and the temperature remains at 0° until all of the solid has disappeared. This temperature is called the freezing point of water.

When one gram of ice melts at 0° C, 79 calories of heat is absorbed, and when the same weight of water freezes, 79 calories of heat is liberated. This heat is called the *heat of fusion* (per gram). The liberation of energy as water freezes is due to the loss of kinetic energy by the molecules when they change to the more closely packed and regular pattern of ice. As ice melts, energy must be absorbed, of course, to tear down the crystal patterns of ice and to give the molecules the added kinetic energy which they possess in the liquid state.

Expansion occurs when water changes into ice. The amount of the expansion is about one eleventh of the volume of the water. This means that each liter of water at 0° becomes 1.09 liters of ice at the same temperature. Because of this expansion, pipes burst when the water in them freezes. For the same reason ice floats on water. An iceberg is a floating mass of ice, and since its density is only slightly less than that of sea water, the greater part of its volume is submerged. The freezing of water in cracks in rocks has much to do with the weathering and crumbling of rocks and the formation of soil. The freezing of water in the soil has an important influence upon the physical properties of the soil. Soil which has been exposed to the freezing and thawing of winter weather is opened up and is made more porous and "mellow." This is at least one reason why fields which are to be planted in the spring are sometimes plowed in the fall.

"Snow" crystals are formed in many beautiful patterns. These are extremely small, but if they were allowed to "grow," they would display common tendencies of development and would produce larger

crystals of identical form. The various lace-like crystals of snow are due to the more rapid growth of the crystal in some directions than in others.

THE CONVERSION OF LIQUID INTO ITS VAPOR

12. Evaporation

Although molecular attraction is far greater in the liquid than in the gaseous state, we cannot think of the molecules of the liquid as at rest. Even in solids, molecules appear to be moving, although their motions are limited to vibrations about fixed points. At a definite temperature, the *average* kinetic energy of the molecules of a liquid is constant, but this does not mean that all of the molecules are moving with the same velocity. If we could examine, at some one instant, the individual molecules within a given volume of liquid, we should certainly find that the velocities of some are considerably greater and of others considerably less than the average. Let us consider a liquid in which the average kinetic energy of the molecules is just about sufficient to balance the attraction that holds them together. The slower molecules are held together more firmly than those that possess the average kinetic energy, but the more rapidly moving molecules are able to overcome the binding effects of this attraction and may escape through the surface of the liquid into the space above. This escape is called *evaporation*.

Since the average kinetic energy of the molecules is thought always to be the same, at a given temperature, the percentage of molecules possessing velocities greater than the average is always the same at that temperature. This means, therefore, that the number of molecules that escape through a definite area on the surface, in the same period of time, is always the same at the same temperature. Hence, the rate of evaporation of a liquid at constant temperature is constant, provided the condition of the space above the surface of the liquid does not change, i.e., the quantity of vapor in a definite volume does not change.

Only the molecules very near the surface of a

liquid at ordinary temperatures have an opportunity to escape. Those that escape must, in reality, have velocities greater than the average velocity of the molecules in the body of the liquid. The latter are pulled equally in all directions, but the former have no molecules above them and are pulled, therefore, toward the center of the liquid. The molecules which escape from the surface must overcome this downward urge. When freed, the molecules act as typical gas particles. If the vessel is open, they diffuse into the surrounding space, and evaporation continues until the liquid disappears.

The molecules that have the greatest velocity are the ones that escape, therefore, the average velocity and the average kinetic energy of the molecules left in the liquid are reduced as evaporation proceeds. Since heat is molecular motion, the quantity of heat energy for a given number of molecules, or weight of water, is also reduced and so, too, is the temperature. Evaporation always results, therefore, in cooling effects.

Evaporation would soon cease, even in an open vessel, if the more slowly moving molecules did not acquire sufficient energy to permit them to escape from the attraction of their fellow particles in the liquid. Evaporation does not cease, however, because heat is absorbed from the surroundings, which are cooled accordingly as a result of the evaporation of the liquid. This cooling effect is used in refrigeration. For such purposes water is not as satisfactory as many liquids, such as ethyl or methyl chloride, sulfur dioxide, or ammonia. These liquids evaporate very rapidly and therefore exhibit greater cooling effects than water.

13. Equilibrium Between a Liquid and Its Vapor

If sufficient liquid in proportion to the space above it is placed in a closed vessel, evaporation does not proceed to completion. In an open vessel the escaping molecules diffuse away into the surrounding space, and only occasionally does one rebound into the liquid as the result of a collision with a

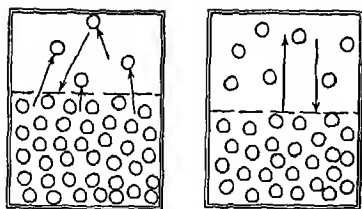


Figure 77

In a closed vessel molecules escape from the liquid into the vapor state. Some molecules of vapor also return to the liquid. Eventually, a state of equilibrium is attained (right).

molecule in the air. Let us consider the case of a liquid which partially fills a closed vessel. The space above the liquid contains some vapor, and this exerts a pressure — called the *vapor pressure* — upon the surface of the liquid and upon the walls of the container. If the space contains air or other gases in addition to water vapor, then the pressure due to the latter is, strictly speaking, the *partial pressure of water vapor*. The molecules which escape from the surface travel in straight lines until they strike the walls of the vessel or until they collide with other molecules. Some of them will be deflected in a direction which carries them back eventually to the surface of the liquid. Here they may be caught and held by the same attractive forces that held them before their escape. The number of particles which return to the liquid depends, evidently, upon the number of molecules in a definite volume of the vapor. At first, this number is relatively small, and the partial pressure of the water vapor is correspondingly small. Hence more molecules escape into the vapor state than return to the liquid in a definite period

of time. The number of molecules of vapor gradually increases, and, with increasing numbers, more and more return to the surface and penetrate into the body of the liquid. Ultimately, a *state of equilibrium* must be attained, when the number escaping, or evaporating, from the liquid is the same as the number returning, or condensing, and hence the relative numbers of molecules in the vapor and liquid remain unchanged as long as equilibrium is maintained. We must not think of either evaporation or condensation as ceasing. They proceed at the same rate, and the equilibrium is dynamic rather than static in character. A molecule on the surface of the liquid at one instant may be a molecule in the vapor state the next instant, but for this molecule, which has changed into the vapor state, another must have returned to the liquid. When the equilibrium condition has been reached, the partial pressure of the water vapor in the space above the liquid reaches its maximum value for a given temperature.

The state of equilibrium may be destroyed by changes of conditions that affect the relative numbers of molecules leaving and returning to the liquid. Thus, the pressure of the vapor is suddenly reduced by removing the cover and allowing expansion to occur. Let us assume that the expansion carries the gas into another vessel placed above the first container (Figure 78). Since the molecules are now scattered through a larger volume, the number striking a unit of area on the surface must be smaller than the number striking the same area before the expansion. The escape of molecules from the liquid proceeds, however, at the same rate as before, and for a time more particles will leave the surface than return to it. This causes an increase in the number of molecules of vapor. Finally, a state of equilibrium will again be established. Since the rate at which the molecules escape has remained unchanged, the new state of equilibrium must be identical with the first, the pressure that the molecules exert upon a

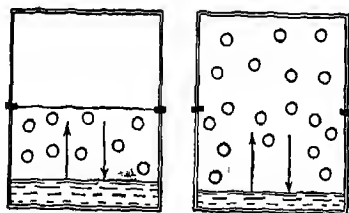


Figure 78

Equilibrium is established again when the space above the liquid is increased.

unit of the surface (or upon the walls) will be the same as before. If the space into which the vapor is allowed to expand is sufficiently large so that all the liquid must evaporate to produce the required number of molecules of vapor, equilibrium cannot be established. But if any liquid, regardless of how much or how little, remains, the *pressure of the vapor (at equilibrium) will always be the same at the same temperature*. If the pressure of the vapor above the liquid is increased, the vapor condenses until the same pressure of vapor per unit of area is exerted as before. Since the pressure of a gas depends only upon the number of molecules striking a definite area and upon their velocity, the extent of the space above a liquid has no influence on the vapor pressure at equilibrium.

14. Vapor Pressure

The vapor pressure *at equilibrium* balances the escaping tendency of the molecules and, in a certain sense, is a measure of what we may regard as the pressure exerted by the molecules in leaving the liquid. This is a definite pressure for a given temperature and a given liquid, it is the *maximum vapor pressure* of the liquid at the temperature specified. Obviously, the vapor pressure is not, under all conditions, equal to this maximum; the pressure of vapor in a vessel containing too little water to produce equilibrium would not be equal to the maximum, or equilibrium, vapor pressure.

The partial pressure of the water vapor in the atmosphere differs from time to time even at the same temperature. There are days in summer when the humidity is high, i.e., the partial pressure of water vapor in the air is almost equal to the pressure of water vapor in equilibrium with the liquid. On such days we are uncomfortable, because water evaporates very slowly from our skin, and we are without the cooling effect of its evaporation.

We are interested usually, however, in the vapor pressure at equilibrium, and it is this

pressure to which we shall refer in future discussions when we speak of the vapor pressure of a liquid, unless some other condition is specified.

15. The Vapor Pressures of Different Liquids

Ethyl alcohol, ether, and similar liquids that evaporate more rapidly than water, at the same temperature, have correspondingly greater vapor pressures at equilibrium between liquid and vapor than water has. The vapor pressure of any readily volatile liquid can be determined by allowing the vapor to come to equilibrium with a small sample of the liquid that is contained above

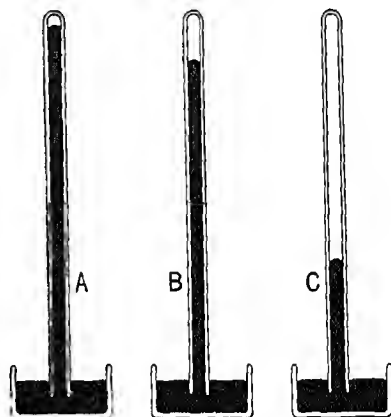


Figure 79 The Relative Vapor Pressures of Water (A), Ethyl Alcohol (B), and Ether (C) at the Same Temperature

the mercury in a barometer tube (Figure 79). The pressure of the vapor depresses the level of the mercury in the tube and can be measured by the difference in levels in two tubes, one containing nothing but mercury, and the other containing mercury and the liquid above it.

VAPOR PRESSURE OF LIQUIDS AT 20° C

Water	17.5 mm
Ethyl alcohol	43.9 mm
Ether	442.2 mm.
Carbon disulfide	298 mm
Chloroform	159.6 mm

Our knowledge of the liquid state leads us to believe that the average kinetic energies of the molecules of *all* liquids are the same at the same temperature. If this is true, the differences in the vapor pressures and rates of evaporation of different substances must indicate that the attraction of different kinds of molecules for molecules of their own kind is not the same but varies widely for different liquids. The smaller the vapor pressure, the greater must be the attraction of the molecules. Molecules of ether, for example, are much less firmly held together than molecules of water.

16. Change of Vapor Pressure with Change in Temperature

An increase in temperature is accompanied by an increase in the velocity and a corresponding increase in the average kinetic energy of the molecules of a liquid. As the temperature rises, therefore, more molecules can break away from the forces that hold them in the liquid, the number of molecules escaping in a definite period of time from a definite area of surface is increased. If equilibrium is to be maintained, a greater number of molecules must, in the same period of time, return to the liquid state. This condition requires, then, that more molecules must exist in the same volume of vapor above the liquid, and consequently that the vapor pressure is increased as the temperature of the liquid increases.

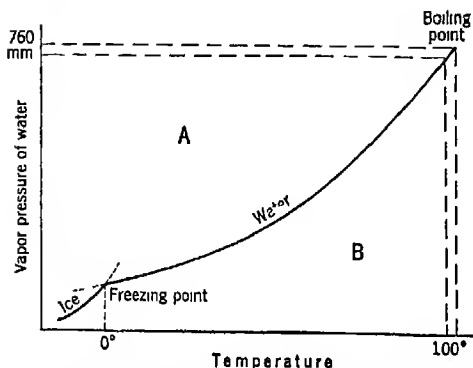


Figure 80 The Vapor Pressure of Water and Ice at Different Temperatures

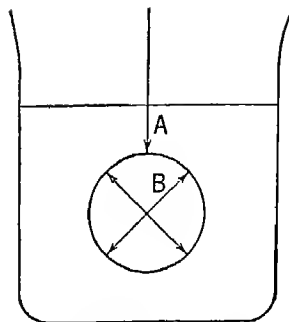


Figure 81 Boiling

In order that bubbles of water vapor may form within the body of the liquid, the pressure inside the bubble must be equal to the pressure upon the bubble. The pressure inside the bubble is the maximum pressure of water vapor at the temperature of the liquid. The pressure from without is the atmospheric pressure plus whatever pressure is produced by the liquid above the bubble. $A = \text{Pressure of atmosphere} + \text{hydrostatic pressure}$, $B = \text{Vapor pressure inside bubble}$.

The relation of the vapor pressure of water and the temperature is shown graphically in Figure 80. At every point along the curve, water and its vapor are in equilibrium. At all points off the curve, there is no state of equilibrium. In the region *B*, water vapor is the stable form, while in region *A*, liquid water itself is stable. For example, water vapor at 50° cannot be kept at a pressure of 600 mm, it will condense to form the liquid. Similarly, the liquid cannot be maintained at a temperature of 80° if the pressure of the vapor above it is less than 355 mm. If the pressure is allowed to remain at some value less than 355 mm, the water will completely evaporate at this temperature.

17. The Boiling Point

If water evaporates in an open vessel, water vapor mingles with the atmosphere because of diffusion, the partial pressure of water vapor is only a small part of the total pressure of the atmosphere. Hence the pressure above the surface of the liquid remains the same, although the vapor pressure of water increases with increasing temperature. Finally, as the temperature rises higher and higher, the vapor pressure becomes equal to the atmospheric pressure. The tempera-

ture at which this occurs is the *boiling point* of the liquid. Further application of heat does not increase the vapor pressure; the heat supplied is used to promote evaporation by supplying more and more molecules with more than the average velocity for this temperature. The temperature remains constant at the boiling point until all the liquid has changed into vapor.

Boiling is indicated by the formation of bubbles of vapor in the body of the liquid and their rise to the surface, where the vapor that they contain mingles with the atmosphere. When a liquid boils, therefore, evaporation occurs not only at the surface but throughout the liquid. Since boiling involves the formation of bubbles, it cannot occur except under conditions favorable to the existence of bubbles. Now, a bubble cannot exist unless the pressure inside it is equal to the pressure upon it from the outside. The pressure inside the bubble is the vapor pressure, the pressure without is the pressure of the atmosphere, plus the pressure exerted by the liquid above the bubble. The latter is very small as compared to the pressure of the atmosphere, which is equal to the pressure of a column of water more than thirty feet in height. Boiling occurs, therefore, only when the vapor pressure of the liquid becomes equal to the pressure of the atmosphere. Actually, as pointed out above, the vapor pressure must be a little greater than this pressure, because of the small additional pressure that the liquid itself exerts upon bubbles within it.

It is evident that the temperature at which water (or any liquid) boils depends upon the atmospheric pressure. Since this pressure varies from day to day in a given locality, the boiling point of water is not the same at all times. The atmospheric pressure also varies with the elevation above sea level. On a mountain top, for example, the vapor pressure of water becomes equal to the external pressure at a lower temperature than it does in a neighboring valley. It is difficult to cook foods in water at high elevations, since the cooking depends upon the temperature which

is obtained, and not upon the boiling of the water. Steam pressure cookers are based upon the principle that a higher temperature must be attained before water will boil under increased pressure. At the higher temperature foods are cooked more quickly.

18. The Boiling Points of Different Liquids

If we draw a broken line across the top of Figure 82 and drop perpendiculars from the points at which it cuts each curve to the temperature co-ordinate, the boiling points of the different liquids will be the temperatures where the perpendiculars fall. The fact that one liquid has a greater vapor pressure at a given temperature than another does not mean that this is true at all temperatures, but, in general, the greater the vapor pressure of a liquid and the more rapidly it evaporates at ordinary temperatures, the lower is its boiling point. Thus, ether with a vapor pressure of 442 mm at 20° C. boils at 35°, and water with a vapor pressure of 17.5 mm at the same temperature boils at 100° C. (760 mm pressure). In comparing the boiling points of different liquids, or of two samples of the same liquid, it is evident that the temperatures must be connected to the temperatures corresponding to the standard pressure or at least to the same pressure.

19. Vapor Pressure of Ice and Other Solids

The molecules in ice must have a much smaller average kinetic energy than those of water. Ice, however, evaporates. Snow crystals disappear at times when the temperature is below the melting point. Since the molecular forces are stronger in a solid than in the corresponding liquid, and since the temperature, and hence the velocity of the molecules, is lower, relatively few molecules can escape from the surface of a solid as compared to the number which escape from the same surface of the liquid state of the same substance. A solid such as ice, however, shows a definite vapor pressure at a given temperature. This vapor pressure increases with rise in temperature as in the

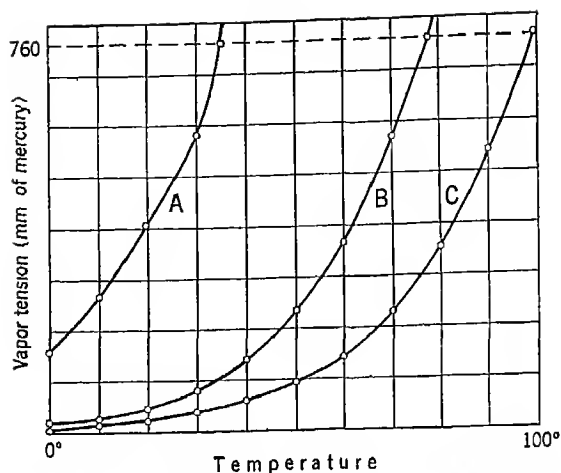


Figure 82 Vapor Pressure Curves for Ether (A), Alcohol (B), and Water (C)

case of a liquid. The rate at which the vapor pressure of ice increases with the temperature is greater than the rate for water (Figure 80). As the temperature rises, the vapor pressure becomes, finally, equal to that of the liquid. The temperature at which the vapor pressures of ice and water are equal is one where the two phases—liquid and solid—are in equilibrium with each other. At this temperature liquid and solid may remain in contact with each other without a change in temperature. This is the *freezing point* of the liquid and the *melting point* of the solid.

If we place a block of ice and a quantity of water in a closed vessel and maintain a temperature of 0°C , each is in equilibrium with the same amount of vapor in the unfilled portion of the vessel. If this were not the case, the phase with the higher vapor pressure would place in the vapor state more molecules than could be in equilibrium with the other, and the vapor would condense to form the latter. Let us assume that ice has the lower vapor pressure at 0° . Then the vapor in a closed vessel containing both water and ice at this temperature would condense to form more ice. There would then be insufficient vapor in the vessel to produce equilibrium with water, more of which would then have to evaporate. There would then be too much for equilibrium with the ice, more of which would form,

and so on, until finally all the liquid would disappear.

20 Surface Tension

We have already (page 169) called attention to the unequal distribution of molecular forces about the molecules at the surface of a liquid. A molecule which lies deep within the body of the liquid is attracted by other molecules which lie all around it and, consequently, the attraction in each direction is balanced by an equal attraction in an opposite direction (Figure 83). But there are no molecules directly above those at the surface. Molecular attraction pulls these molecules back into the liquid, and there is no compensating upward pull. Because of this unequal distribution of forces, molecules are removed from the surface, i.e., the surface tends to become smaller. The result would be the same if the surface were under a tension. Hence, we speak of the *surface tension* of a liquid. As the result of the tendency of its surface to shrink, a small mass of liquid assumes a spherical shape, since a sphere has a smaller surface than any other form of the same weight of the substance.

The surface tension of a liquid decreases as the temperature rises. A decrease in surface tension corresponds to an increase

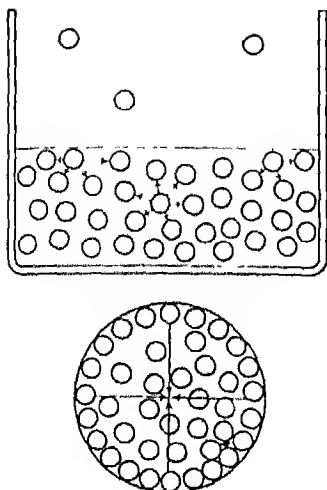


Figure 83

Diagrams showing the cause of surface tension and explaining why a small mass of a liquid takes a spherical form.

in surface, and this change calls for the expenditure of energy, since more molecules must be separated from the particles in the body of the liquid and removed to the surface. The energy required is applied as heat, and the increase in temperature is represented by the increased velocity and kinetic energy of the molecules.

Since the molecular attraction is overcome entirely by the speed of the molecules at the critical temperature, the surface tension disappears entirely at this temperature. We may regard the critical temperature as the point at which the gas can be compressed without liquefaction, to a volume of the same size as that which the liquid would occupy. The failure of the gas to liquefy above the critical temperature is due, of course, to the speed of its molecules, which is great enough to overcome completely the molecular attraction, regardless of the pressure which may be used in forcing the molecules closer together.

21. Viscosity

The molecules of a liquid exert attraction for one another, and hence we should expect that there is within the liquid itself a certain resistance to the movement of molecules

over and around one another, a movement usually described as *flow*. This resistance is expressed in terms of the *viscosity* of the liquid and is usually measured, in comparison with a standard liquid such as water, by the rate at which the liquid flows under constant pressure through a long capillary tube held in a vertical position.

The viscosities of water, alcohol, and ether are relatively small as compared with those of glycerine or lubricating oils. The former are mobile liquids, and the latter are highly viscous or less mobile. The viscosity of a liquid depends upon the average distance separating the molecules, the size of the molecules, and their average velocity. It increases as the temperature of the liquid decreases. As the temperature of the liquid is lowered some viscous liquids change into plastic solid states, e.g., paraffin and beeswax. The viscosity of lubricating oils is a very important factor in determining their value, and the viscosities of certain solutions and mixtures are important in several industries, e.g., paint, varnish, and lacquer.

NATURAL WATERS

22. Impurities Found in Water

The water of springs, wells, lakes, rivers, and the sea contains varying amounts of substances either in solution or as solids in suspension. Even "rain water," before it comes into contact with the earth, has dissolved gases and has taken up particles of dust from the atmosphere. Drops of rain are probably often formed about dust particles, which act as nuclei or centers for the condensation of water vapor. The content of water on the earth's surface, or from below the surface, depends upon the nature of the soil and the rocks with which it has come into contact. The impurities present in such waters may consist of the following classes of materials:

(1) Finely divided solids in suspension, these include sand, clay, organic material (bits of plants), and organisms, such as bacteria.

(2) Dissolved salts, these are largely the chlorides, sulfates, and bicarbonates of sodium, potassium, calcium, magnesium, and iron

(3) Dissolved substances of an organic character, these result from the decay of vegetation

(4) Dissolved gases, such as ammonia, carbon dioxide, oxygen, and nitrogen

The suspended solids can be removed in large part from water by filtration. If the clear water is then evaporated to dryness, some idea of the quantity of dissolved solids can be obtained. One liter of water yields, upon evaporation, something like 0.2 to 0.5 g of residue. The water from some wells and from many springs shows a much larger quantity of dissolved salts. If the quantity of these salts is very great, the water is called a *mineral water*. Sea water contains approximately 3.5 per cent of solids, of which about 75 per cent is sodium chloride. The water from salt-lakes (Great Salt Lake, Dead Sea, etc.) contains from 20 to 25 per cent of dissolved solids, most of which is salt.

Water that contains salts of calcium and magnesium is said to be *hard*. Everyone knows that soap does not lather well in hard water. An ordinary soap is a salt of sodium with one of the organic acids that are found, combined with glycerine, in fats. When the sodium salts of these acids are placed in water containing calcium or magnesium salts, they react by double decomposition with the latter, and insoluble calcium or magnesium soaps are formed. Enough sodium soap must be added to remove all the calcium or magnesium from the water before a lather can be produced. Hard waters can be *softened* before use by removing the dissolved compounds of calcium and magnesium.

Hard waters are also objectionable in boilers. Here the salts of calcium and magnesium are deposited upon the walls as the water is changed into steam. As this deposit thickens, loss of the full value of the fuel used to heat the boiler results, because of the thick layer of material that separates the water from the source of heat. The boiler

wall must be heated to a much higher temperature than would be required, or would be possible, if the water were in direct contact with it.

Some waters are also objectionable because they contain dissolved substances, such as the carbonates of sodium and potassium, which produce foaming in boilers. Other substances may cause unpleasant odors and tastes. Still others, notably compounds of iron, may produce stains upon clothing in the laundry. Some waters are unpalatable because of the bad taste which comes from the algae (certain plants) that grow in them. Other waters are dangerous sources of disease because they contain certain types of bacteria, such as the typhoid bacillus.

23. Water for Domestic Use

It is not sufficient that water intended for drinking purposes should be cold, clear, and sparkling. It may be all of these and still be as deadly dangerous as any potion of poison. Even water from a muddy stream may be safer for drinking purposes than clear water from a shallow well or from a stream polluted with sewage. The danger lies not in suspended inorganic material or in dissolved salts or gases, as a rule, but in the presence of disease-producing bacteria, which, of course, cannot be seen without the aid of the microscope. Typhoid, paratyphoid, and dysentery are the most common diseases contracted by drinking contaminated water. The bacteria producing these diseases almost always enter the water in sewage containing waste materials from persons suffering from the diseases.

The chemical examination of water intended for domestic use is concerned primarily with the detection in the water of certain kinds of compounds that may have entered it in sewage. These compounds contain nitrogen and are products of the decomposition and oxidation of proteins. Faulty early in these changes, the nitrogen appears as ammonia, NH_3 , or as compounds closely related to it, later the nitrogen is converted into

nitrites, which contain the NO_2^- ion; and finally *nitrates*, containing the NO_3^- ion, are produced. The change from one of these compounds to the next is promoted by the action of certain bacteria that use the substances contained in sewage as food materials. In water containing sewage that has only recently entered the water supply, most of the nitrogen will be found by chemical examination to be in the ammonia form. This water may be dangerous, because the contamination is of recent origin, and there is a plentiful food supply for bacteria. If the examination shows that the nitrogen is largely in the form of nitrates, the water may be regarded as fairly safe, the pollution must have occurred at a time considerably previous, and the food supply of bacteria likely to be found in sewage will have been exhausted. Water showing more than 0.01 part of nitrite ion per 1,000,000 parts of water is not regarded as safe without treatment to kill bacteria. The chemical analysis usually shows, also, the quantity of chlorine that is present as chloride ion in a definite quantity of water. Some chlorine is to be expected in natural waters, but the normal quantity is known for different parts of the country, and the presence of excessive amounts (usually as salt) is considered as fairly conclusive evidence of contamination by sewage, because almost the only source of chlorine is sewage containing excretions of the human body.

The bacteriological examination of water is usually more definite than a chemical analysis. In making such an examination the usual procedure is to count the number of bacterial colonies which develop upon a "culture" that is treated with the water. Each bacterium in the water sample which is placed upon the "culture" produces a colony. The bacteria detected in this manner are those that are found in sewage of human origin and although usually harmless themselves, their presence in water indicates that there has been pollution by sewage which may contain other dangerous

types of bacteria. Contrary to a somewhat general opinion, the bacteriologist does not examine water for definite evidence of the presence of any individual disease-producing type of bacteria. Water to be used for drinking purposes should be checked frequently by bacteriological examinations. The fact that such an examination gives water from a certain source a clear record does not mean, of course, that this water will remain pure.

24. The Purification of Drinking Water Supplies

The domestic water supplies of cities may come from rivers, lakes, springs, wells, or from basins which gather the "run-off" from the surrounding soil. None of these sources can be regarded as safe, regardless of precautions to exclude sewage. In fact, contamination of the supply by sewage is usually recognized, and proper methods of purification are necessary. The bacteria in water may be killed by boiling for a few minutes, but "boiled water" is unpalatable, because it contains none of the dissolved gases that natural waters contain in solution. Nearly pure water can also be obtained by distillation; solids, both dissolved and suspended, are left behind in the distilling flask when the water changes into vapor, but dissolved gases escape and when the water vapor condenses again to the liquid, air and other gases that may be present again dissolve, unless precautions are observed.

Because of the small scale upon which they can be operated, it is obvious that boiling and distillation cannot be used as practical methods of purifying water except in isolated cases and for individual needs. The purification of the water supply of a community must employ methods that can produce millions of gallons daily.

Usually both filtration and chemical treatment are practiced. Dissolved salts and gases are not removed. Bacteria are either killed by the addition of certain chemicals, or removed along with other suspended ma-

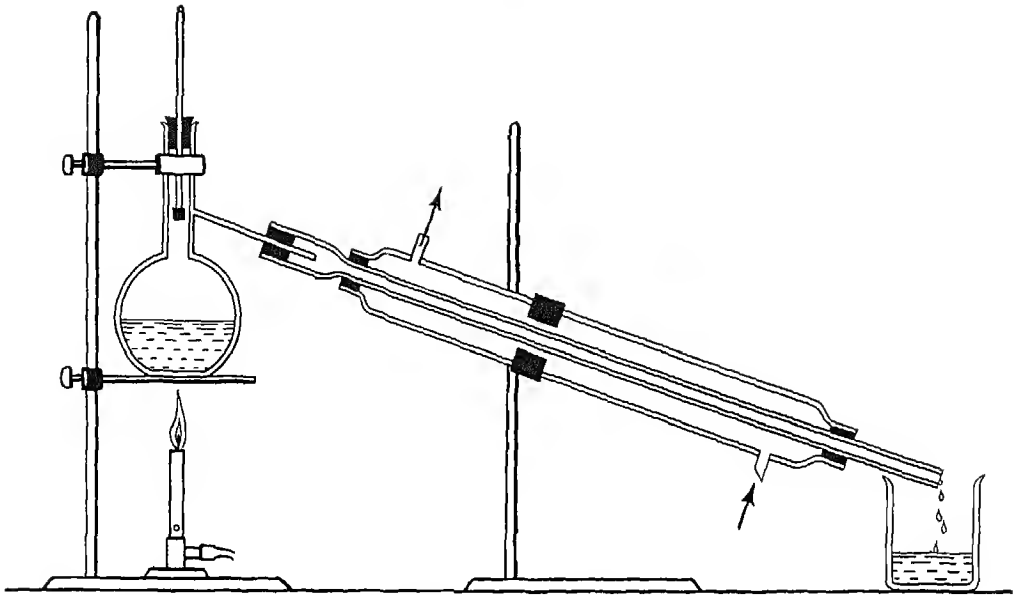


Figure 84 Distillation of Water

Dissolved and suspended solids can be separated and practically pure water obtained by distillation
Cold water is passed through the jacket of the condenser to convert steam into the liquid

terial by filtration. If the water contains much mud, clay, or sand, it is first allowed to stand in a settling basin where most of this material settles out. It then passes through the filter, which consists of layers of sand and gravel. The filter may be designed to allow the water to pass through slowly or rapidly. In rapid filters, the beds of gravel and sand are shallow, and coarse material is used. Settling basins are almost always employed in connection with rapid filters to remove most of the suspended material, which otherwise would collect in the filtering beds and retard the passage of water. These rapid filters are not as efficient as the slow ones in removing bacteria, but they do act very satisfactorily in removing suspended soil and substances which discolor the water. The complete removal of bacteria is not necessary if the water is disinfected by chemical treatment. A high-speed filtration plant can be operated to produce about 125,000,000 gallons of filtered water daily per acre of surface. This is almost 50 times as much water as can be obtained from a slow filter bed of the same surface.

Substances that produce objectionable odors and tastes in the water supply may be removed by aeration, by filtering the water through beds of granular charcoal, or by mixing finely divided, activated carbon with the water and later removing it by filtration. Odors and tastes caused by adding too much chlorine can be removed by adding small amounts of a substance such as sodium sulfite that reacts with the chlorine, or with compounds of that element that may have been produced in the water.

The construction of a filter bed designed for slow filtration is shown in Figure 85. The seepage of water through the sand leaves behind the mud, clay, and other suspended material including most of the bacteria. The slime which gathers on the surface of the sand aids materially in increasing the efficiency of the filter. The growth of algae on the sand is sometimes encouraged to further aid in removing organisms. The water which finally emerges from the lower layers of gravel finds its way into drain pipes made of porous tile. Through these pipes it is led to the pumping station from which it is forced out into the city's mains.

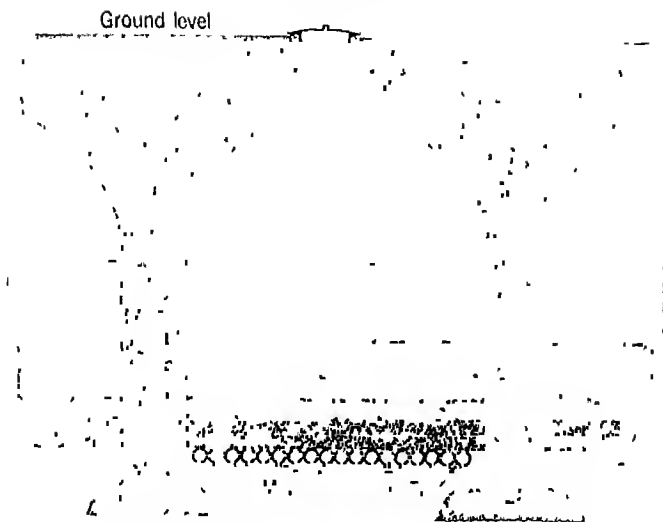
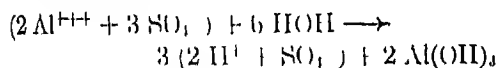


Figure 85 The Construction of a Filtration Bed
A, water; B, fine sand; C, D, E, coarse sand and gravel

Aluminum sulfate is often added to water in the settling basins or filters. This substance reacts with water to form aluminum hydroxide, a gelatinous solid, which settles, carrying with it the suspended material and many bacteria.

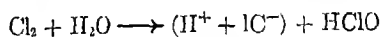


Calcium hydroxide, $\text{Ca}(\text{OH})_2$, is usually added along with the aluminum sulfate. When this is done, calcium sulfate, CaSO_4 , instead of sulfuric acid is produced. Ferrous sulfate, FeSO_4 , sodium aluminate, NaAlO_2 , and alum are sometimes used in place of aluminum sulfate.

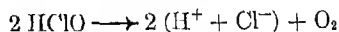
25. Purification of Water by Chemical Treatment

The use of chlorine to kill bacteria in water is now a common practice in almost every community of any size in this country and in most other countries. Chlorine is used for this purpose because of its efficiency, its low cost, and the small quantity that is required. Not more than one part of chlorine is required to kill all the bacteria in a million parts of water.

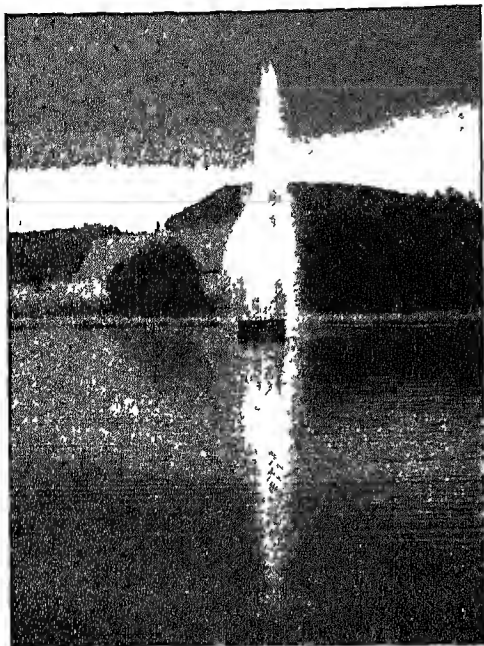
The use of chlorine for the disinfection of water in this country dates from about 1913. Prior to that time bleaching powder (CaOCl_2) had been used in many places. The effect of chlorination has been most pronounced in the reduction of the death-rate from typhoid fever. In many cities this death-rate has been reduced by 75 per cent or more immediately after treatment with chlorine has been started. The chlorine which is added gradually reacts with water, forming first hydrochloric acid and hypochlorous acid.



The latter slowly decomposes:



Bacteria which enter the water after the chlorine has disappeared will not be killed. The efficiency of chlorine also depends upon the quantity of other organic matter in the water, since organic material is also acted upon by chlorine or by the oxygen which is released when chlorine reacts with water. Probably the safest procedure is to chlorinate water by adding enough chlorine to destroy all organic material with which chlorine will react. Any excess of chlorine remaining can be removed by dechlorination before the water is used. This is a process in which harmless substances which react with chlorine are added to the water.



Courtesy of Atlas Powder Company

Figure 86 The Reservoir of a City's Water Supply
Aeration is used in purification of water because it aids in the oxidation of organic materials

Some waters which contain substances derived from coal-gas plants and certain other kinds of factories develop unpalatable tastes after chlorination. These tastes are due to the chlorinated products of some of the substances which find their way into the water from these wastes. Water may also extract similar substances from leaves and other forms of vegetation. The bad taste of water is most often caused, however, by certain kinds of plants (algae) which grow in the water of reservoirs. These plants may appear in the water in greater numbers at certain seasons. Their presence is recognized when the water has a fish-like taste. Algae are usually killed by adding a trace of copper sulfate to the water in the reservoir.

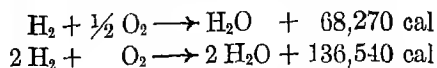
THE CHEMICAL PROPERTIES OF WATER

Not only does water play a direct rôle in many reactions in which it is itself converted into other compounds, but it also

exerts a profound influence upon the reactions of other substances

26. The Stability of Water

Water is a relatively stable compound. When it is formed by the combination of its elements, considerable heat is liberated. When one gram-molecular weight (18 grams) of water is produced by the combination of hydrogen and oxygen, and the water vapor produced is condensed and cooled to 25°, 68,270 calories of heat is liberated:

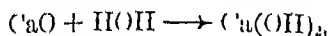


When 18 g of water is decomposed, a similar quantity of energy must be consumed in the process. This energy may be supplied by heat. Even at a very high temperature, heat decomposes water only slightly. If water vapor is heated in a closed tube at a definite temperature for some time, a portion decomposes to form oxygen and hydrogen. The decomposition ceases after a time, or, at least, the amounts of water vapor, oxygen and hydrogen reach definite values that remain unchanged as long as the temperature is constant, a state of equilibrium is attained, and the oxygen and hydrogen combine at the same rate as water vapor decomposes. The reaction is said, therefore, to be reversible and in this respect resembles the reaction between steam and iron (page 109). At 1500° C, less than 0.2 per cent of the water vapor is decomposed in attaining equilibrium. As the temperature increases, the percentage of undecomposed water vapor in the equilibrium mixture gradually decreases, but even at 2000° C, only about 1.5 per cent, and at 2700° C, only about 11 per cent is decomposed. Compounds that are not readily decomposed by heat even at considerably elevated temperatures are said to be stable. Upon this basis of distinction, water is *stable*.

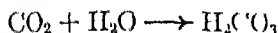
27. Reaction of Water with Oxides, Salts, and Other Substances

We have previously (page 69) referred to

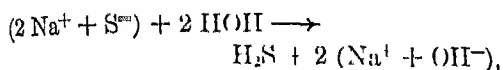
the reaction of water with the oxides of the metallic elements to form hydroxide-bases,



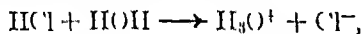
and with the oxides of non-metallic elements to form acids



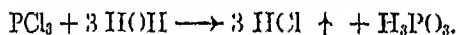
Water itself acts both as an acid and a base. In the reaction,



water reacts as an acid, it supplies hydrogen ions, or protons, that react with the sulfide ions, S^{2-} , of sodium sulfide to form hydrogen sulfide, H_2S . In the reaction,



water accepts protons and acts as a base. It also reacts, by double decomposition or exchange, with certain covalent substances such as phosphorus trichloride, PCl_3 , that cannot be classified as salts (page 162)



If only a small quantity of water is added, it is consumed in the reaction, and the hydrogen chloride escapes as a gas, because there is no water in which it can dissolve. Reactions of this kind and those of water with salts, such as sodium sulfide, are frequently classified as examples of *hydrolysis* — double decomposition or exchange reactions in which one of the substances involved is water.

28. Water as an Oxidizing Agent

The great stability of water indicates that this substance will not give up readily the oxygen which it contains to other substances. For this reason water is not regarded as a good oxidizing agent, although almost 90 per cent of it (by weight) is oxygen. Very powerful reducing agents, however, can reduce it. Thus, we have shown (page 75) that magnesium will burn in an atmosphere of steam, forming magnesium oxide and liberating hydrogen. This is a case of oxidation, in which magnesium is oxidized and hydro-

gen is reduced. Hydrogen's valence number is reduced to zero, and magnesium's is increased from zero to +2. Steam also oxidizes hot iron, forming the magnetic oxide of iron and hydrogen (page 111). Steam which is passed over or through red-hot carbon (coke) is converted (page 111) into carbon monoxide and hydrogen in the production of water gas. These are also cases of oxidation. Iron and carbon are oxidized, and hydrogen is reduced. Since water is the substance that brings about the increase in the valence of magnesium, iron, and carbon, in these reactions, it must be regarded in all of these cases as the oxidizing agent. Since the valence number of hydrogen is 1 in water, and since hydrogen exhibits no greater combining capacity, water does not have any reducing action on any oxidizing agent.

29. Hydrates

Many compounds, ions, and even free elements combine with water to form compounds in which *molecules of water* are united by shared electron pairs with molecules, ions, or atoms of the other substance. These compounds are called *hydrates*. Sulfuric acid, for example, forms a hydrate when it is mixed with water; the formation of the new substance, the hydrate, is indicated by the large quantity of heat that is evolved when the concentrated acid is poured into water.

Many hydrates are compounds of salts and water, although there are also hydrates of acids and of hydroxides, many ions in aqueous solution also exist as hydrates as, for example, the hydronium ion (page 155), which really is nothing more than a hydrated hydrogen ion, $\text{H}^+ \cdot \text{H}_2\text{O}$.

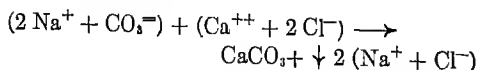
Dry or anhydrous calcium chloride, which is used to remove the water from various gases, is represented by the formula CaCl_2 . Its efficiency as a drying agent is due to its tendency to combine with water to form the hydrate $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. A solution of calcium chloride in water gives, upon evaporation, crystals of this hydrate. The crystals of "blue vitriol" (CuSO_4) are composed of the hydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Other examples of

hydrates are: $\text{CrCl}_3 \cdot 4 \text{H}_2\text{O}$; $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$; $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, and alum, $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24 \text{H}_2\text{O}$

In each of these formulas the period () is used to indicate the chemical combination of water with the salt. Since these are all ionic compounds ($\text{Ca}^{++} + 2 \text{Cl}^-$, for example), the water is actually combined with one or both of the ions of each compound.

The formula of the hydrate of sodium carbonate is written as $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, instead of $\text{Na}_2\text{CH}_{20}\text{O}_{13}$, because the latter would indicate, contrary to fact, that the carbonate ion, CO_3^{--} , loses its identity in the hydrate.

The carbonate radical is as real a part of the hydrate as it is of the unhydrated salt. The water combined with the salt in the hydrate does not appear to be firmly held, and when the hydrate is dissolved in water, the water "of hydration" appears to be no different than the water in which the salt dissolves. Dissolved sodium carbonate reacts in double decompositions, for example, as if composed only of sodium and carbonate ions, and its reactions are the same, regardless of whether the substance placed in the solution is the hydrate ($\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$) or the unhydrated salt (Na_2CO_3). The identical behavior in solution may be due, however, to the fact that only one of the two substances (the hydrate) exists in solution. Since the salt that crystallizes from the solution is the hydrate, the chances are that it is this form, or at least some hydrated form, which exists in the solution. We have no definite method of determining the extent to which substances of this kind are hydrated in their solutions. For this reason, the water combined with a substance in solution is usually not indicated in the formulas that are used in writing equations for reactions in which the substance takes part. Thus, the reaction between calcium chloride and sodium carbonate in a solution which has been prepared from $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ is written as



At ordinary temperatures, solid hydrates and the corresponding anhydrous salts possess very different properties. Different hydrates of the same salt also have different

properties — different melting points, colors, specific gravities, and different solubilities in various solvents. Anhydrous cupric sulfate, for example, is white; but the pentahydrate, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, is blue. Cobalt chloride is blue when anhydrous, but the hydrate, $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, is red. Anhydrous chromium chloride, CrCl_3 , is pink, but the hydrate, $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$, is green or violet. Some hydrates are sufficiently stable so that they can be mixed and heated; they can thus be made to react without first being converted into the anhydrous salts. In such reactions the hydrates of the same salts display some differences in properties from one another and from the anhydrous salts. Because of all of these differences in properties, and because of their definite composition, hydrates must be regarded as true compounds.

30. Hydrates, Hydroxides, and Oxygen Acids

It is important that we distinguish between (1) hydrates and (2) hydroxides and acids that contain oxygen. Thus, calcium hydroxide and sulfuric acid may be formed by allowing water to react with calcium oxide and sulfur trioxide, respectively. Furthermore, both of these compounds liberate water when they are heated to a sufficiently high temperature. Nevertheless, they cannot be regarded as *hydrates* of the oxides. In acids, the hydrogen of the original water molecules acts independently of the oxygen when the acid is in solution. In hydroxides, under similar circumstances, each of the hydrogen atoms acts *with* an oxygen atom to form the hydroxyl radical (OH). The water which reacts with the oxides to form these compounds appears, therefore, to lose its identity and to become a more intimately related and united part of the compound than the water in hydrates.

31. The Structure of Hydrates

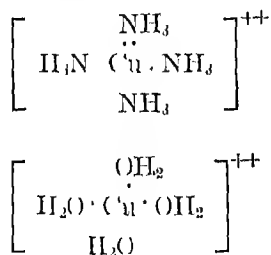
The valence numbers are not changed when elements, radicals, or ions combine with water to form a hydrate. It is obvious, therefore, that the water of a hydrate is held

in chemical combination by bonds other than those of the usual ionic or covalent type

Several substances form compounds analogous to the hydrates formed by water. Among such substances are ammonia, alcohol, and others that contain the OH or NH₂ group. Each of these compounds contains an atom having one or more pairs of electrons not used in forming bonds with atoms in its own molecule. Thus, in the molecule of ammonia one pair of electrons belonging to the nitrogen atom is free or unused, and in water two pairs of electrons of the water molecule are free



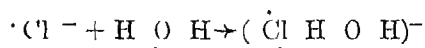
The metallic ion of a salt has no electrons in its outermost electron group because these electrons were lost when the atom became an ion. Thus the cupric ion, Cu⁺⁺, contains no electrons in the outermost group of the atom, although this group, as in other atoms, can hold eight (and sometimes more) electrons. The cupric ion can acquire enough electrons to build up a stable group in the valence shell by sharing pairs of electrons which are free, or unused, and which belong to atoms of oxygen in water or to atoms of nitrogen in ammonia



The hydrated cupric ions produced by such reactions have the same charge and valence number as the unhydrated cupric ion, because the molecules of water themselves have no charges, and hence produce no change in the charge of Cu⁺⁺. Water is attached to the cupric ion by co-ordinate

covalent bonds (page 146) just as it is attached to a proton in the hydronium ion (page 155)

In some hydrates the hydrogen atoms of water molecules may form co-ordinate covalent bonds with atoms having unused pairs of electrons that hydrogen atoms may share. Thus the hydrogen atom of a water molecule may form a bond with a chloride ion.



A bond of this kind may account for another method by which the water of some hydrates is held in chemical combination. Similar bonds may be formed by water molecules and an oxygen atom of a sulfate ion. Since hydrogen atoms act as the connecting links by which water molecules are bound to other particles, such bonds are called *hydrogen bonds*.

In some hydrates, water molecules may merely be held within unfilled and open spaces of the crystal lattice. In other hydrates, the crystal is somewhat like ice in which the ions are dissolved.

The water of a hydrate was spoken of at one time as "water of crystallization" — a term based, no doubt, upon the fact that many salts crystallize from water solutions as hydrates. If this water is removed from the crystals, by exposure to the air or by heat, they crumble, and the substance becomes a powder. Water is not necessary, however, for the formation of crystals. Many substances, such as potassium chlorate and sodium chloride, form crystals, but they have no hydrates — at least, not in the solid state. Furthermore, salts that form crystalline hydrates may also crystallize when they are not combined with water. Thus, copper sulfate will form crystals of CuSO₄ in concentrated sulfuric acid, which combines with the water and prevents the formation of the hydrate of the salt. It is also possible to form hydrates that do not possess crystalline structures. For example, an aqueous solu-

tion of sulfuric acid is most certainly a mixture of water and a hydrate of the acid or its ions.

32 Other Examples of Hydrates

Some acids and a few bases which are solids at ordinary temperatures form hydrates. Among these may be mentioned the hydrates of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$, and barium hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$. Many minerals are hydrated in their natural states. Asbestos, talc, soapstone, and mica are hydrated magnesium silicates. Carnallite, an important mineral because of its potassium content, is $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. Schoenite is $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$.

33. The Formation and Decomposition of Hydrates

Let us consider a hydrate in a closed vessel (We shall assume that there is no water vapor in the space above and surrounding the hydrate.) At a definite temperature, a certain number of molecules escape from the surface of the hydrate in a unit of time. The condition is very much like the evaporation of a liquid. At the same temperature, the number of molecules escaping from the surface of different liquids varies with

the attraction of the different kinds of molecules for one another. For this reason, different liquids have different rates of evaporation, different vapor pressures, and different boiling points. Now, the water in some hydrates is more firmly held than in others. This corresponds to the different molecular attractions in liquids. As in the evaporation of liquids, the molecules of water that escape from the surfaces of hydrates into the surrounding space (in a closed vessel) may also return to the solid and combine to form the hydrate again. The rate of return depends, evidently, upon the number of molecules in a definite volume of this space, i.e., upon the aqueous vapor pressure. At first, this vapor pressure is very small, but it increases as more and more molecules escape into the vapor state. Finally the number returning becomes equal to the number escaping in the same period of time. When this condition is reached, we may think of a state of equilibrium as existing between the rate of decomposition and the rate of formation of the hydrate. As long as the vessel remains closed, the quantity of water combined in the hydrate will remain constant. If the vessel is opened, the hydrate continues to decompose until only the anhydrous salt is left, if the space in which the hydrate is exposed is free of water vapor. The atmosphere, however, is not free of water vapor. Although the amount varies from day to day and from place to place, water vapor is always present and exerts a variable vapor pressure, which is, of course, a part of the total pressure.

Some hydrates, at ordinary temperatures, will give up to the atmosphere the water that they contain. This occurs because the vapor pressure of these hydrates is greater than the vapor pressure of the moisture in the air (Figure 87). Crystals composed of hydrates with high vapor pressures are likely to crumble when they are exposed to the air. They are said to *effloresce* and the change is called *efflorescence*. In perfectly dry air, all hydrates are efflorescent, since dry air has no

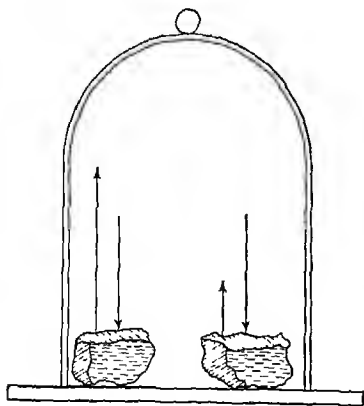


Figure 87

The downward pointing arrows represent the aqueous vapor pressure of the atmosphere, and the arrows pointing upward represent the aqueous vapor pressures of the two hydrates. The crystal on the left will lose water to the air, that on the right will not.

aqueous vapor pressure to offset even a slight vapor pressure of the hydrate.

Other hydrates have very small aqueous vapor pressures, smaller even than the partial pressure of the water vapor in the atmosphere. These hydrates are stable in the atmosphere at ordinary temperatures (Figure 87). If the corresponding anhydrous salts are placed in the air, the moisture in the air will combine with the salts.

The aqueous vapor pressure of a hydrate increases as the temperature rises. Hence, a hydrate which is efflorescent at room temperature loses its water of hydration even more readily at higher temperatures. A salt which combines with the moisture in the air to form a hydrate at ordinary temperatures can be heated to a temperature at which it no longer does so.

When more than one hydrate of a salt exists, each has its own definite vapor pressure at a given temperature. If the hydrate which has the higher vapor pressure is heated to a temperature at which its tendency to lose water is greater than the tendency of water to form the hydrate, this hydrate — which is usually the one containing the larger percentage of water — will decompose, leaving the more stable hydrated form of the substance. If heated to a still higher temperature, the second hydrate may also be decomposed. Conversely, if an anhydrous salt which forms more than one hydrate is exposed to the air, the hydrate which forms depends upon the temperature and the partial pressure of the water vapor in the atmosphere. Thus, the pentahydrate of copper sulfate, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, loses water when it is placed in a current of warm air, and is converted, first, into the trihydrate, $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$, then into the monohydrate, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, and finally, into the anhydrous salt. If a current of moist air is passed over the anhydrous salt, the changes are reversed, with the ultimate production of the pentahydrate.

Plaster of Paris, $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$, is produced by heating gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, at a temperature of about 125°C . At this temperature the lower hydrate is stable. When plaster of Paris is mixed with water to form a plastic mass, the lower hydrate combines with water to form gypsum once again. The formation of gypsum crystals and the removal of the water results in the hardening or "setting" of the plaster. The setting of Port-

land cement also depends upon the hydration of different substances in the mixture.

34. Deliquescence

When crystals of ionic compounds are placed in moist air, some water will condense to form a film of moisture on the surface. If the ions of the crystal have a tendency to form hydrates, such substances will be produced by combinations between the ions on the surface of the crystal and water. If the aqueous vapor pressure of this hydrate is small as compared with the partial pressure of the water vapor in the air, moisture will continue to condense, and this water will dissolve the salt, if it is soluble, forming a saturated solution. If the pressure of the water vapor in the air is still greater than the aqueous vapor pressure of the solution, water will continue to condense, diluting the solution and thus allowing more and more of the salt to dissolve. In some instances, solution is complete. Thus, grains of anhydrous calcium chloride form drops of a solution of calcium chloride when they are exposed to the air. Substances which act in this manner to remove moisture from the air, thus forming aqueous solutions, are said to be *deliquescent*. Deliquescence cannot be regarded as the reverse of efflorescence, because it involves, fundamentally, the formation of solutions. Only soluble substances — and not all of them — undergo deliquescence in moist air.

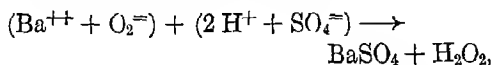
Table salt does not become moist and, therefore, does not "cake" in its container if it contains nothing but pure sodium chloride, which is not deliquescent. The tendency of some samples of salt to become moist is caused by small quantities of impurities which are deliquescent.

HYDROGEN PEROXIDE

35. Peroxides

The compound, H_2O_2 , belongs to a class of substances which are composed of oxygen and a second element, and which are called

peroxides Barium peroxide, BaO_2 , and sodium peroxide, Na_2O_2 , are other examples of substances belonging to this group. In all of these compounds the $-\text{O}_2$ group acts as a radical and possesses a valence of -2 . Thus, when BaO_2 reacts with sulfuric acid,

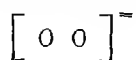


the $-\text{O}_2^{=}$ radical displays a behavior very much like that of the sulfate ($\text{SO}_4^{=}$) radical. The peroxides differ in this respect from ordinary oxides which react with acids to form salts and water. Since the $\text{O}_2^{=}$ group acts as a divalent radical, it is apparent that the valence of hydrogen in hydrogen peroxide is the same as in water, and that of barium in barium peroxide is the same as in the oxide, BaO . There are oxides, such as MnO_2 and PbO_2 , which resemble the peroxides only with respect to their formulas. These are dioxides rather than peroxides. The valence of manganese and lead in these compounds is actually 4, and the oxides react with acids to form water, not hydrogen peroxide.

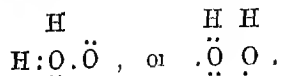
36. Structure

Hydrogen peroxide was discovered in 1818 by Thénard, who was interested in detecting differences in the reactions of various oxides with acids. In the course of his studies, he happened to use one of the oxides which we now recognize as a peroxide, and when he did so, hydrogen peroxide (a new substance at this time) was formed instead of water. The combining proportions of hydrogen and oxygen in hydrogen peroxide show twice as much oxygen as there is contained in water for the same weight of hydrogen. Its simplest possible formula, therefore, is HO , but since it appears to contain the radical $-\text{O}_2^{=}$, its real formula must be H_2O_2 .

In terms of the electron theory of valence, a peroxide contains oxygen linked to oxygen

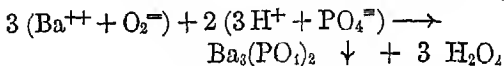
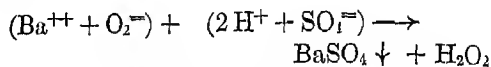


Hydrogen peroxide has one or both of the following structures

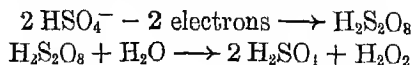


37. Preparation

A dilute solution of hydrogen peroxide in water may be produced by the action of an acid upon the *peroxide* of a metal. It may be produced, for example, by the action of hydrochloric acid upon sodium peroxide, but a more nearly pure solution of hydrogen peroxide is produced by the reaction of barium peroxide with sulfuric or phosphoric acid

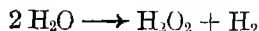


Barium sulfate and barium phosphate are only slightly soluble and can be separated from the solution of hydrogen peroxide by filtration. For industrial use, hydrogen peroxide is produced by the electrolysis of a solution of dilute sulfuric acid or a solution of ammonium bisulfate, NH_4HSO_4 . Peroxydisulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$, is first formed at the anode, and then reacts with water at somewhat elevated temperature to form hydrogen peroxide and sulfuric acid



Dilute solutions of the peroxide can be concentrated to a certain extent by distillation under reduced pressure.

Hydrogen peroxide is also produced in small amounts when some metals are oxidized in moist oxygen, and when water is exposed to ultra-violet light



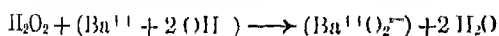
These methods, however, are not of importance as means of obtaining the substance for use.

38. Properties

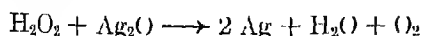
Above its melting point (-17°C) hydrogen peroxide is a liquid of syrupy consistency. It is colorless in thin layers, but appears slightly blue when observed in thick layers. As compared with water, its density is 1.47 times as great. Its boiling point (1 atmosphere) is 151.1°C .

Chemically the substance is characterized by its limited stability. It decomposes very readily into water and oxygen. This change proceeds at a rate which depends upon the concentration, the temperature, and the presence of certain catalytic substances. The pure compound is likely to decompose spontaneously and explosively. Decomposition is very slow at room temperature in dilute solution. For this reason, it is usually supplied and used as a 3 per cent solution. This solution usually contains a small amount of an acid or an organic compound (often acetanilide), which acts as a negative catalyst. A base, such as sodium hydroxide, acts as a positive catalyst in the decomposition. Finely divided platinum, manganese dioxide, silver, saliva, and blood also accelerate the decomposition.

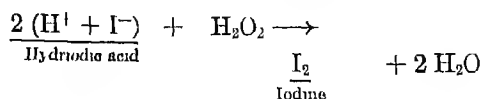
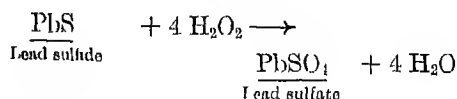
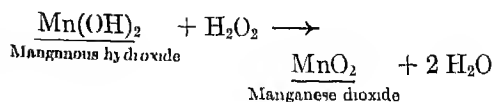
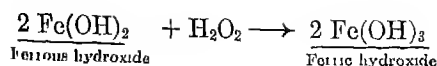
Hydrogen peroxide acts as a very weak dibasic acid. By *dibasic acid* is meant one which contains two replaceable atoms of hydrogen per molecule. In aqueous solutions it forms HO_2^- (perhydroxyl) ions. The peroxides of the metals are salts of this acid. Thus, when hydrogen peroxide reacts with a solution of barium hydroxide, the peroxides of barium and water are formed.



With some substances which are very vigorous oxidizing agents hydrogen peroxide acts as a reducing agent. For example, it reacts with silver oxide, Ag_2O , to form free silver, water, and oxygen.



The following reactions are typical of those in which hydrogen peroxide acts as an oxidizing agent.



39. Uses

Because of the ease with which it decomposes, hydrogen peroxide is a vigorous oxidizing agent, and is frequently used as a bleaching agent for silk, wool, and hair. It is also used as a germicidal agent and antiseptic. It is often used as an oxidizing agent in the laboratory. A solution containing 30 per cent of hydrogen peroxide is now available for commercial uses. Hydrogen peroxide has also been used to supply oxygen for combustion in rockets operated by jet propulsion.

40. Test for Hydrogen Peroxide

Hydrogen peroxide can be detected by means of a reaction involving potassium dichromate. A very dilute solution of the dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is added to the solution which is to be tested for the peroxide. The solution is then acidified with sulfuric acid and ether is added. Ether does not mix to any great extent with water and is lighter, hence it forms the layer on top. Hydrogen peroxide and the dichromate react to form a blue substance (perchromic acid) which is more soluble in ether than in water. When the mixture is shaken, the ether layer dissolves the product of the reaction and is colored blue. Because the perchromic acid is unstable, the blue color soon fades.

Review Exercises

1. A large anship will hold about 6,500,000 cu

- ft of gas If we assume standard conditions, what volume of water would have to be electrolyzed to produce the hydrogen required to fill it? (1 cu ft = 28.32 liters)
- 2 If a mixture containing 500 ml. of oxygen and 2200 ml of hydrogen is exploded, which gas and what weight and volume (at standard conditions) of it will compose the residue? What weight of water will be formed?
 - 3 In one of Morley's experiments he found that 3.2559 g of hydrogen combined with 25.8531 g of oxygen. How do these weights compare with the *average* combining weights of the two elements?
 - 4 Describe a method which can be used to measure the vapor pressure of a liquid at different temperatures.
 - 5 Why do all liquids not have the same vapor pressures at the same temperature?
 - 6 Describe the equilibrium that results between a liquid and its vapor in a closed vessel. How do changes in temperature affect this equilibrium?
 - 7 Explain the cooling effect of evaporation, the cooling effect of melting ice, and the heating effect of condensing vapors and freezing liquids.
 - 8 Why must heat still be applied to continue the boiling of a liquid which has been heated to its boiling point?
 9. Why do bubbles of vapor form in a boiling liquid? Why do they not form below the boiling point?
 - 10 Explain the nature and cause of the surface tension of a liquid.
 - 11 What weight of water, at 100° C., could be completely evaporated by the heat that is liberated when 10 pounds (1 lb = 453.6 g) of water freezes?
 - 12 Why is the temperature not likely to change rapidly near a large body of water?
 - 13 By what experimental method could you determine whether a liquid is water or a solution of hydrogen peroxide without determining the composition of the liquid?
 - 14 What is the maximum (standard) volume of oxygen that can be obtained from 10 liters of a 3 per cent solution of hydrogen peroxide, if the specific gravity of the solution is 1, and if none of the water is decomposed?
 - 15 The following are some of the important terms and expressions that have been used in this chapter. Define them and explain them by the use of appropriate examples or illustrations: calorie, maximum density of water, heat of fusion, vapor pressure, boiling and freezing points, hydrolysis, hydrate, anhydrous salt, efflorescence, deliquescence, peroxide.
 16. What weight of hydrogen peroxide can be produced by treating 500 g of barium peroxide with sulfuric acid?
 - 17 What weight of water is contained in one pound of sal soda, or washing soda, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$?
 18. A sample of hydrated magnesium sulfate (Epsom salts) weighing 15 g was heated until all the water was expelled. The anhydrous magnesium sulfate weighed 7.32 g. What is the formula of the hydrate?
 - 19 What evidence shows that hydrates are definite compounds?
 - 20 How does a hydrate differ from a hydroxide?
 - 21 Why should manganese dioxide, MnO_2 , not be called manganese peroxide?
 - 22 How does the water of the human body aid in the regulation of the body's temperature?
 - 23 How does water react with aluminum sulfate and sodium sulfide?
 - 24 Give an example of a reaction in which water acts as an oxidizing agent. Why does water not act as a reducing agent?
 - 25 What are the different kinds of impurities found in natural waters? What are the sources of these impurities?
 - 26 What impurities are objectionable? Why are they objectionable?
 - 27 Why is anhydrous calcium chloride sometimes placed on roads?
 - 28 How would you explain his loss to a grocer who bought washing soda, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, at 8 cents per pound, stored it in an open bin, sold it at 10 cents per pound, but lost money?
 - 29 Why is sulfuric acid preferred to hydrochloric acid in preparing hydrogen peroxide from barium peroxide?
 - 30 The maximum quantity of oxygen is produced by decomposing the hydrogen peroxide in one

kilogram of the solution usually sold by a pharmacy. What is the maximum quantity of water that can be produced from this oxygen?

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SOLUTIONS

Corpora non agunt nisi soluta (Substances do not react unless they are dissolved)

AN ALCHEMIST OF THE FIFTEENTH CENTURY

1 Introduction

The tendency to form solutions is an extremely important physical property of many substances, and the solutions which are formed play important rôles in many different varieties of chemical change. Many reactions which are extremely slow, when the pure substances are mixed, are very rapid if the reacting substances are first dissolved in water, or some other medium, and are then mixed. The increase in speed results from better contact in solution, where molecules, or other minute portions, of different substances are mingled.

We have already referred to the importance of solutions in life processes. We have seen that the oxygen we breathe must dissolve in water before it can be used by the body. We have stated that digestion consists essentially of processes in which foods, such as starches, fats, and proteins, are converted into substances that will dissolve in the blood. Mention has also been made of the oxidation of worn-out body tissues to form soluble substances that can be eliminated from the body. We may recall also that the composition of natural waters depends largely upon the substances that these waters have dissolved from the air and earth. The action of these waters in forming solutions, together with chemical action and mechanical erosion, is one of the important processes that convert rocks into soil, alter the soil's fertility, and are, in general, responsible for changes in the geological status

of the earth. Many minerals have been deposited from solution, and enormous quantities of sedimentary rocks (limestone) were laid down originally as deposits of calcium carbonate from substances previously in solution in the waters of seas and oceans.

THE NATURE OF SOLUTIONS

2 Evidence That Solutions Are Mixtures

In the first chapter it was said that materials could be divided into two classes, substances — elements or compounds — and mixtures. Since it is obvious that a solution cannot be an element, it must be classified as either a compound or a mixture. The several reasons why it should not be classified as a compound may be summarized as follows:

(1) The composition of a solution is not definite. Thus, we may dissolve one gram or ten grams of salt in 100 ml of water. Solutions of water and alcohol may contain the two substances in any proportions, we can dissolve 1 ml of alcohol in 100 ml of water, and we can dissolve 1 ml of water in 100 ml of alcohol. Usually, however, there is an upper limit to the quantity of one substance that will dissolve in a definite quantity of the other, but it is possible to prepare a solution of any composition within this limit. This variation of composition, alone, is sufficient reason for excluding solutions from the classification of compounds.

(2) The properties of a substance are not greatly altered when it dissolves, and the changes that occur are temporary and physical instead of

chemical When a solid dissolves in a liquid, for example, the solution is a liquid, hence it is necessary to think of the physical state of the solid as having been changed, for evidently there is no longer a solid state. Sometimes there are certain indications that the components of a solution do react to form new substances. Obviously, there is a chemical change when a piece of zinc disappears in a solution of hydrochloric acid; the evolution of a gas is sufficient evidence that something more than a mere mixing of zinc, hydrogen chloride, and water is occurring. If the substances that are mixed undergo chemical changes, this is another matter and cannot be regarded as the formation of a simple solution of the original substances. For most solutions we can disregard chemical changes and consider them simply as mixtures in which particles of the different substances mingle freely without suffering any change in composition.

Sugar, for example, when dissolved in water still possesses the properties of sugar, and although water's physical properties and behavior are modified somewhat, its chemical properties are not affected by the presence of the sugar in any fundamental sense, it will still react with the same substances as pure water to form the same products.

(3) Finally, the freezing point and boiling point of a solution are not constant. The boiling point of a solution of sugar and water, for example, varies with the composition of the solution.

Furthermore, solutions containing equal molecular quantities of many different substances in the same weight of a solvent freeze and boil at the same temperature. This fact indicates that it is the solvent — water, for example — that freezes and boils in a solution — not the solution as a whole — and that the freezing and boiling points of the solvent are changed in the solution by an amount depending upon the number — not the kind — of molecules that dissolve.

3. Mixtures That Are Not Solutions

A solution is defined, therefore, as a mixture, but it is evident that it is a particular kind of mixture. A solution of salt in water, for example, differs markedly from a mixture of sand and water. In the latter the sand settles, collecting in the lower part of the containing vessel and leaving the water on

top comparatively clear. On the other hand, the salt in a solution never settles. Furthermore, the water can be separated from the sand by pouring the mixture into a funnel fitted with a folded filter paper. The water passes through, and the sand is left on the paper. When a solution of salt in water is filtered, however, the salt passes through the paper along with the water. Some mixtures which pass through filters are not solutions. Thus, a mixture of water and very finely divided clay will pass through a filter paper. If we examine this mixture with the aid of a microscope, we may observe the particles of clay, but we cannot see the particles of a substance dissolved in water, whatever aids to our vision we may employ. The mixture of clay in water is an example of a finely divided *suspension* in water. Eventually, the suspended material settles to the bottom of the container.

The suspension in water of particles too small to be observed with even the most powerful microscope can be easily demonstrated (Figure 88) by passing a beam of light into the mixture. Small particles of the solid, which cannot ordinarily be seen, catch the light in the beam and reflect it in all directions, thus becoming visible when observed at right angles to the direction of the beam. If the mixture contains no such particles, the beam passes through it without suffering any reflection. Suspensions of material even more finely divided than the clay, which we find sometimes in water, can be detected by this method. These are called *colloidal suspensions* (Chapter 35). Solutions, however, do not display this phenomenon when a light beam is passed into them. We must, therefore, conclude that the particles which they contain are much smaller than particles of substances which are only suspended in the liquid. Investigations of the magnitudes of the particles forming colloidal suspensions show that some of these correspond to clusters, or aggregations, of relatively few molecules as compared with particles which can be observed by the eye.

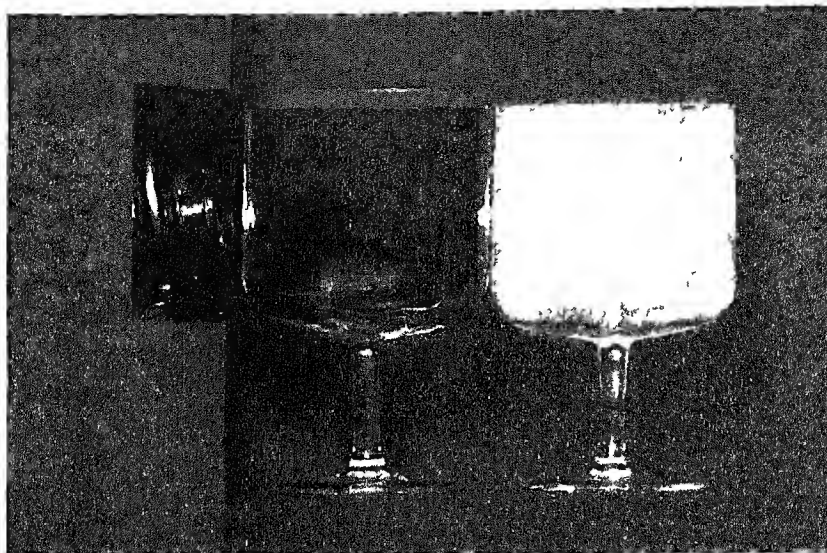


Figure 88 The Passage of a Beam of Light Through a True Solution (left) and Through a Colloidal Suspension (right)

alone or even with the aid of a microscope. The still smaller particles of a solution, therefore, must have approximately the dimensions of individual molecules or ions.

4 Definition of a Solution

A mixture of sand and water or one of sugar and sand is *non-homogeneous*. This means that one sample removed from such a mixture is not exactly like another sample. The two components are not distributed uniformly throughout the mixture. Even the suspension of finely divided clay in water shows differences in composition in different parts of the mixture, more clay particles are likely to be found near the bottom than near the top. The composition of a solution, however, is apparently *homogeneous*. If we place a lump of sugar in a beaker full of water, the solution is of course not immediately homogeneous. As long as the lump at the bottom of the beaker continues to dissolve, the solution in the immediate vicinity of this solid will contain more sugar than the upper portion, the sugar diffuses throughout the solution but not as rapidly as it dissolves. When the solid has disappeared, or when as

much of it as will has dissolved, the solution then, after a time, becomes homogeneous, and a sample removed from near the surface will be found to contain the same quantity of sugar per ml. as a sample removed from the bottom or halfway down.

A solution may be defined as an apparently homogeneous mixture of two or more kinds of molecules, ions, or groups of molecules. If we could examine the individual particles that compose the mixture we should find that they are of different composition, and hence the solution is not actually homogeneous in the sense that it is composed of identical particles of matter. The proportions of the substances that are mixed to form a solution can be varied only without certain limits in most cases. There are solutions, e.g., a solution of ethyl alcohol and water, in which the relative quantities of the components can be varied indefinitely. For most substances, however, there is a definite limit to the quantity that can be dissolved in a definite quantity of water or some other substance. It should be noted that not all solutions of sugar and water, for example, have the same composition, nevertheless, a sample of *one*

solution of sugar in water has the same composition as any other sample of that solution, provided the components have been thoroughly mixed, or the solution has been allowed to stand until the sugar has diffused throughout the volume of the solution.

The homogeneity of a solution is thought to be the result of the continuous and random motion of the molecules of the substances that form the solution. As in the case of gases, this leads eventually to an intimate mixture, in which the number of each kind of molecule per unit of volume is determined by the total number of each kind in the mixture and by the volume that the mixture occupies.

5. Components of a Solution

The components of a solution are referred to as the *solvent* and the *solute*. The former is the component of the mixture which is present in the greater amount. We may also think of the solvent as the medium in which the particles of the solute are scattered and which has the same physical state as the solution. Sometimes, however, it is impossible to say which of the components should be called the solvent and which the solute. This question arises, for example, in a solution of water and alcohol containing 50 per cent of each. The terms are used only for convenience and there is no fundamental difference between them.

6. Classes of Solutions

When we think of solutions, we usually have in mind solutions of solids in liquids. But since a solution is defined as a homogeneous mixture, it is evident that solutions are not limited to this one group of mixtures. Theoretically, we should be able to produce the following kinds of solutions, which are distinguished by differences in the physical state of the solute and solvent.

- | | |
|------------------------|-----------------------|
| (1) Gases in gases | (6) Solids in solids |
| (2) Gases in liquids | (7) Solids in liquids |
| (3) Gases in solids | (8) Liquids in gases |
| (4) Liquids in liquids | (9) Solids in gases |
| (5) Liquids in solids | |

The nine classes of solutions are illustrated by the following examples.

(1) All mixtures of gases are solutions, since they are homogeneous. Air, for example, may be regarded a solution in which oxygen, nitrogen, and the inert gases are homogeneously mixed.

(2) "Soda water" is a solution of carbon dioxide. Since the gas reacts to some extent with the solvent, the solution contains, also, carbonic acid. The water that we drink contains oxygen, nitrogen, and carbon dioxide in solution. The solubilities of various gases in water are shown in Table 6, page 195. The solubility of a gas is usually expressed as the number of cubic centimeters or grams of the gas which dissolves in 100 cc of water (or another liquid) at a definite temperature and pressure.

(3) The hydrogen occluded by platinum and palladium may be thought of as dissolved in the metals.

(4) Water and ethyl alcohol are miscible in all proportions. Alcohol and ether likewise mix in all proportions, but water and ether form solutions containing relatively small quantities of ether in large quantities of water, or small quantities of water in large quantities of ether.

(5) Mercury dissolves in copper to form a solution of a liquid in a solid.

(6) Metals may diffuse into one another. If a piece of lead is tightly clamped against a piece of gold, the gold will be found, after considerable time, to have diffused into the lead and the lead into the gold. If a sheet of zinc is coated with copper, the zinc diffuses into the copper and changes its color, and the copper diffuses into the zinc. A solution of a solid in a solid is called a solid solution.

(7) Solutions of solids in liquids are well known. More than any other kind of solution, they are employed in bringing about chemical reactions between different substances.

(8) Solutions of liquids in gases are rare and their positive identification as solutions is difficult. We might regard a mixture of air and water vapor as such a solution, since at the temperature of the air water is normally a liquid.

(9) Solutions of solids in gases are also unfamiliar. A mixture of air and sulfur vapor comes as near being a solution of this kind as any that can be cited.

CONDITIONS THAT INFLUENCE SOLUBILITY

7. Effect of Pressure

The only solutions in which the quantity of the solute that dissolves in a definite volume of the solvent is appreciably influenced by the pressure are those involving gases. *The weight of any gas that dissolves in a definite volume of a liquid is directly proportional to the pressure that the gas exerts above the liquid at a constant temperature.* This is Henry's law. For every gram of a gas that dissolves in 100 ml of water, when the pressure of the gas on the surface of the water is one atmosphere, 10 g will dissolve if the pressure is increased to 10 atmospheres, temperature remaining constant. The effect of pressure may be modified somewhat if a chemical reaction occurs between the gas and the solvent.

The most familiar example of the effect of increased pressure upon the solubility of a gas in a liquid is "soda water" and other carbonated beverages. The quantity of gas that dissolves in a definite volume of the liquid is increased by forcing the gas into the liquid under pressure. When the solution is bottled, the cap prevents the escape of carbon dioxide and maintains the pressure. When the cap is removed, the gas escapes, since it is not as soluble when the pressure is reduced.

If a mixture of gases is brought into contact with a liquid, or is bubbled through the liquid, the solubility of each gas is proportional to its partial pressure. Each gas dissolves to the same extent as it would, at the same pressure, if the others were not present, provided that the different gases of the mixture do not react in any way to form new substances. When air is bubbled through water, only about 20 per cent as much oxygen dissolves as would dissolve if pure oxygen, at the same pressure, were used instead of air. This is because the partial pressure of the oxygen in the air is only 20 per cent of the atmospheric pressure.

The solubility of a gas in a solid also depends upon the pressure. But the "solubility" of one gas in another gas is of course independent of the pressure factor. If two gases are mixed, the volume is the sum of the volumes of the individual gases, provided that the pressure is constant; and if the volume is constant, the total pressure must be the sum of the pressures of the individual gases.

Pressure may play an important part in the solution of solids in molten materials and in other liquids deep down in the earth. The crystallization of these substances from their solutions is also influenced by various conditions of pressure. This is a subject, however, about which we know but little at present, because it does not lend itself easily to laboratory experiments. Increase in pressure appears to increase the solubility of some solids and decrease the solubility of others. In all cases the effects of pressures of ordinary magnitude are slight as compared with the effects of other conditions such as temperatures.

8 The Effect of Temperature

(1) *Solutions of Gases in Liquids* The quantity of gas that dissolves in a given weight or volume of a liquid decreases as the temperature of the liquid rises. Bubbles of air collect on the inside walls of a pitcher of cold water that is left to stand in a warm room, indicating that more air is dissolved in the cold water than will dissolve at a higher temperature. If the liquid is raised to the boiling point, all the dissolved gas is expelled along with steam. Variations in the solubilities of different gases in water with changes in the temperature are shown in Table 6.

(2) *Solutions of Liquids in Liquids* Some liquids will dissolve in water in all proportions at all temperatures below their own boiling points and that of water. Among these liquids are ethyl and methyl alcohols, glycerine, and sulfuric, acetic, and nitric acids. Other liquids, such as gasoline and carbon disulfide, do not dissolve in appreci-

TABLE 6

Solubility (in Grams) of Gas in 100 Grams of Water (Pressure, 760 mm)

Gas	0°	10°	20°	40°	60°	80°	100°
Nitrogen	0.00294	0.00231	0.0019	0.0014	0.0011	0.00066	0.0000
Oxygen	0.00695	0.0054	0.00434	0.0036	0.00227	0.0014	0.0000
Hydrogen	0.00019	0.00017	0.00016	0.00015	0.00012	0.00008	0.0000
Carbon dioxide	0.335	0.232	0.169	0.126	0.058		
Hydrogen sulfide	.707	0.511	0.385	0.236	0.148	0.076	0.0000
Sulfur dioxide	22.83	16.21	11.28	5.41			

able quantities at any temperature. Still others, such as ethyl acetate, bromine, and ether, dissolve slightly or moderately at ordinary temperatures. Liquids of the third class dissolve in smaller quantities as the temperature rises, provided that they are relatively volatile. As the temperature rises, their vapor pressure and therefore their tendency to escape into the vapor state increase. If the liquids are not readily volatile, the effect of temperature upon their solubility is more complex and varies for different liquids.

9. Vapor Pressures of Mixtures of Liquids Fractional Distillation

The vapor pressure of a mixture of two liquids, *A* and *B*, varies at a specific temperature with the composition of the mixture. Depending upon the nature of *A* and *B*, this variation may (1) be a gradual, regular change from the vapor pressure of *A* to that of *B* (*a* in Figure 89a), (2) pass through

a minimum for some definite composition of the solution (*b*); or (3) show a maximum value (*c*) for a specific proportion of *A* and *B*.

The boiling point of a solution containing two liquids is the temperature at which the total vapor pressure of the mixture becomes equal to the pressure of the atmosphere. The boiling points of a mixture for which the vapor pressure varies regularly with composition (*a* of Figure 89a) lie along a straight line that connects the boiling points of the two pure liquids. For those mixtures that show minima and maxima of vapor pressures (*b* and *c*, Figure 89) for definite compositions of the solutions, the boiling point curves also pass through minima or maxima.

Let us consider a mixture of two liquids for which the vapor pressure varies with composition as shown by *a* (Figure 89a). This mixture (Figure 89b) boils at a temperature slightly above the boiling point of the lower boiling component, *B*. The vapor produced at the lowest boiling point contains

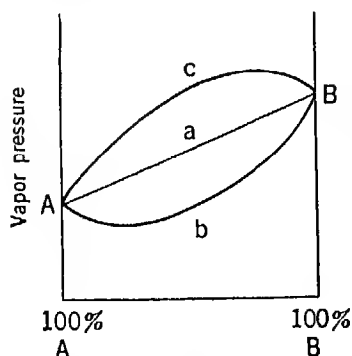


Figure 89a

Vapor Pressure at Constant Temperature of a Mixture of Liquids

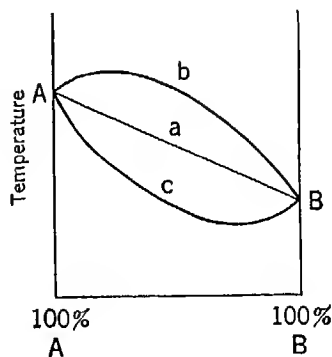
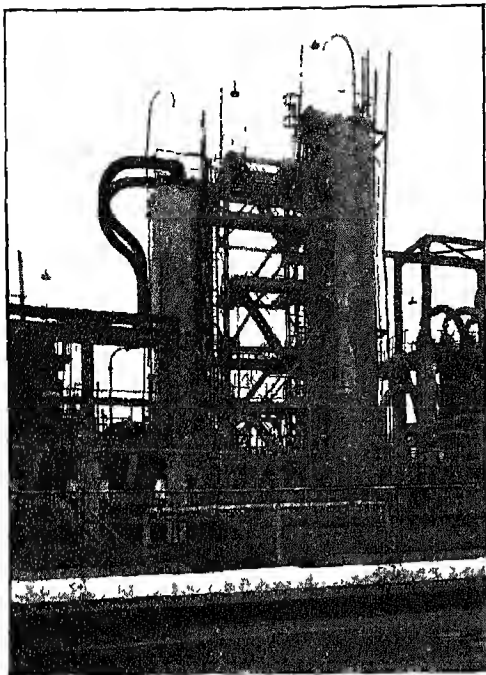


Figure 89b

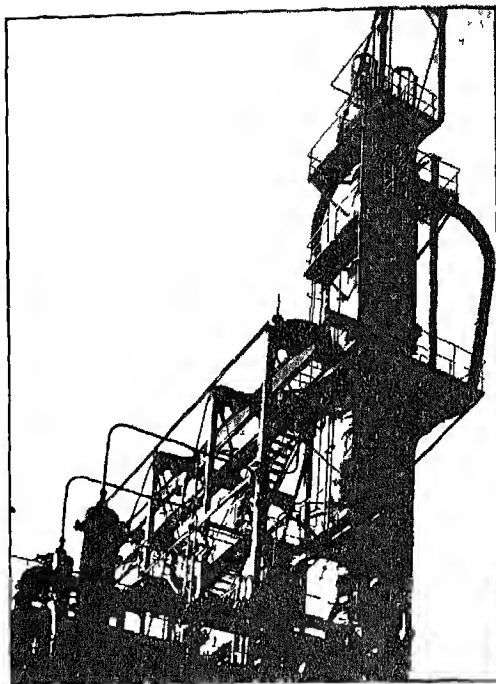
Boiling Temperatures at Constant Pressure of a Mixture of Liquids



Courtesy of the Gulf Refining Company

Figure 90

Towers Used in the Fractional Distillation of Petroleum Products



Courtesy of the Gulf Refining Company

Figure 91

both components but is richer in the lower boiling component than the original mixture. The composition of the mixture is changing continually, and this means that the boiling point also changes. This change is always toward the higher boiling substance, *A*. The vapor contains, therefore, more and more of this component, as the boiling temperature rises, and less and less of the more volatile component. If the vapor is condensed in different fractions, corresponding to different boiling points, the first fraction will be richer in one component (*B*) and the last fraction in the other (*A*). The first and last fractions may be collected and subjected separately to a second distillation in order to obtain another fractional separation of the vapors evolved at different temperatures. If this process is repeated several times, relatively pure samples of the two liquids are eventually obtained. Because of the separation of the distillate (or condensate) into fractions, this process is called *fractional dis-*

tillation. It is used, for example, in producing solutions of alcohol which contain larger relative amounts of alcohol than the solutions resulting directly from fermentation processes. It is also used to separate the components of other liquid mixtures, such as the mixtures of hydrocarbons found in crude oil.

10. Constant Boiling Solutions

When a concentrated solution of hydrochloric acid is heated to the boiling point, the vapor which is formed contains a large amount of hydrogen chloride. The solution remaining in the distilling flask therefore contains a greater percentage of water than at first, and the percentage of hydrogen chloride decreases as boiling continues. The temperature at which the solution boils changes also, becoming higher even than the boiling point of water. Finally, when the percentage of hydrogen chloride becomes 20.24, the mixture boils at a constant tem-

perature and produces vapor of the same composition as the liquid which remains in the still. This is called a *constant boiling solution*, it represents the concentration of the solution which has the lowest vapor pressure and the highest boiling point of all the possible concentrations of solute. For the solution of hydrogen chloride, the constant boiling temperature, at a pressure of 760 mm, is 110° . The composition of the constant boiling mixture varies slightly with the atmospheric pressure.

If a very dilute solution of hydrogen chloride is distilled, the first distillate consists principally of water. The solution which remains in the distilling flask becomes richer in hydrogen chloride, until the percentage of 20.24 and the constant boiling temperature of 110° are attained. It will be observed that the boiling point is higher than the boiling point of either pure component. Pure nitric acid boils at 86° . The constant boiling mixture with water boils at 120.5° and contains 68 per cent of HNO_3 .

Constant boiling solutions are sometimes prepared for use in analytical work, when a solution containing a definite weight of the solute in a definite volume of solution is desired. It is obvious that such solutions can be prepared only for volatile substances, such as hydrochloric and nitric acids. The constant boiling solution gives a definite concentration of the acid, which can be reduced to any lower concentration that may be desired by dilution with water.

11. The Effect of Temperature upon the Solubility of Solids in Liquids

While the maximum quantity of most solids which dissolves in a definite quantity of a given liquid increases with rising temperature, this is not always true. The same rise in temperature may cause great increases in solubility in some cases, slight increases in others, and decreases in still others. Thus, a change of temperature from 0° to 72° causes a change in the maximum quantity of potassium nitrate which will dissolve in 100 g of water from about 12 g at 0° to 140 g at

72° . For sodium chloride the change is from 36 g at 0° to about 38 g at 70° and 39 g at 100° . For calcium hydroxide the quantity which dissolves at 100° in 100 g of water is 0.08 g, while at 20° the maximum quantity that dissolves in the same quantity of water is 0.165 g.

The variations in the solubility of different substances with changes in temperature are shown by the curves of Figure 92. For most of these substances the curves are smooth, indicating gradual changes in solubility as the temperature changes. In certain instances, however, sharp breaks occur in the curves. In the case of sodium sulfate, for example, the solubility first rises as the temperature increases, but at a temperature slightly above 30° , the solubility begins to decrease. This temperature (32.4° exactly) is the transition point at which the hydrate, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, and anhydrous sodium sulfate, Na_2SO_4 , are in equilibrium. If a solution that contains as much sodium sulfate as will dissolve is evaporated at temperatures below 32.4° , crystals of the hydrate are formed. At higher temperatures, crystals of the anhydrous salt are produced, indicating that the hydrate is not stable at these temperatures. Since two substances are involved, and since their solubilities vary differently with the temperature, there are two solubility curves for sodium sulfate, one for the hydrate and one for the anhydrous salt. Similarly, the breaks in the curves for the solubility of calcium chloride indicate (1) transition of the hexahydrate, $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$, to the quadrihydrate, $\text{CaCl}_2 \cdot 4 \text{H}_2\text{O}$, at 30° , and (2) transition of the quadrihydrate to the dihydrate, $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$, at about 45° .

12. Fractional Crystallization

Differences in the variations of the solubility of different substances with the temperature are used in separating the soluble components of a mixture. Let us consider, for example, a solution of potassium nitrate and sodium chloride in water, this solution is actually a mixture of potassium, sodium, nitrate, and chloride ions. When the water is removed by evaporation, we might expect crystals of any one or of all four substances

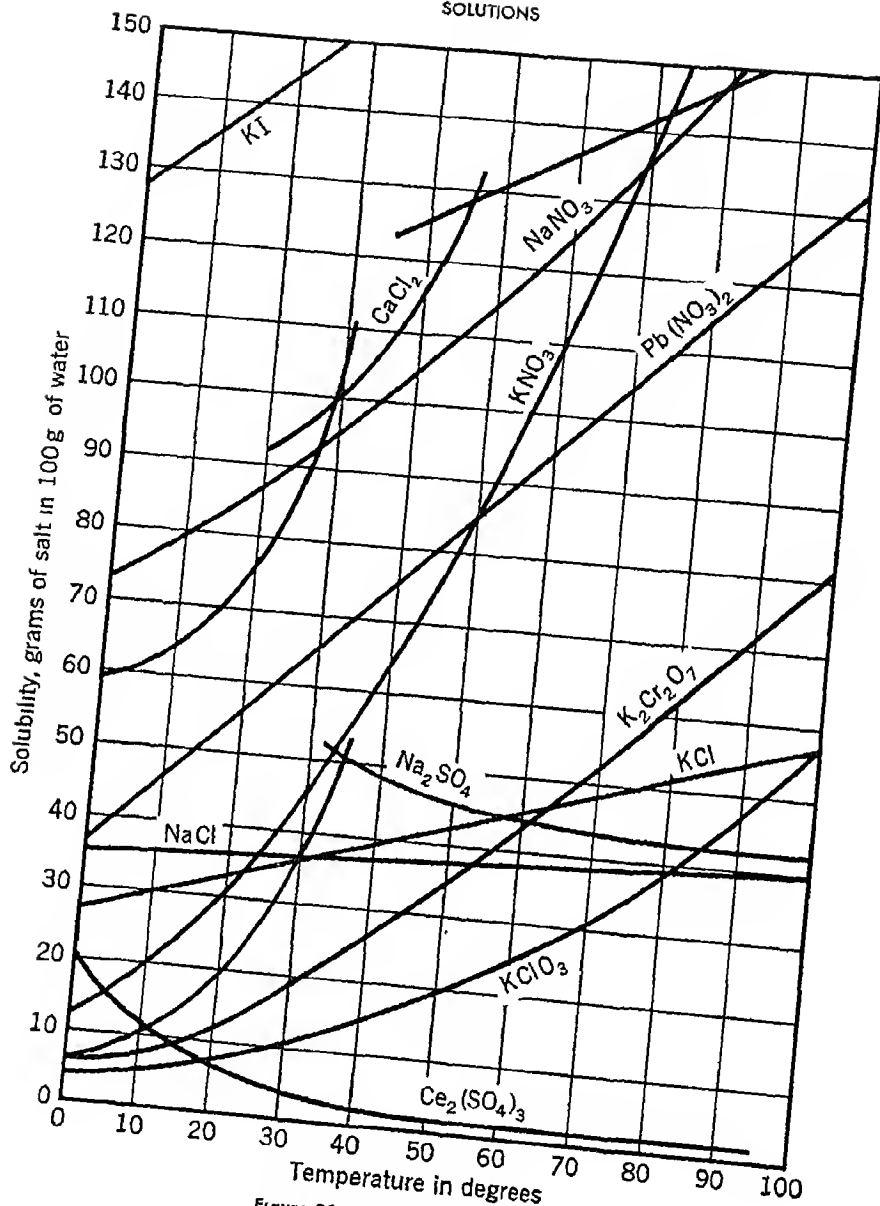


Figure 92. Solubility Curves
Showing the variation of solubility with temperature

to be produced —KCl, NaCl, KNO₃, and NaNO₃.

A concentrated solution is made by dissolving as much potassium nitrate and sodium chloride as possible, at 100° C, or by evaporating a less concentrated solution at this temperature until crystallization begins

The crystals that form at this temperature are composed of sodium chloride, which is the least soluble of the four substances at 100°. The crystals are removed by filtration, and the filtrate is cooled to a low temperature, let us say to 0°. The solubility of potassium nitrate drops from 246 g at 100°

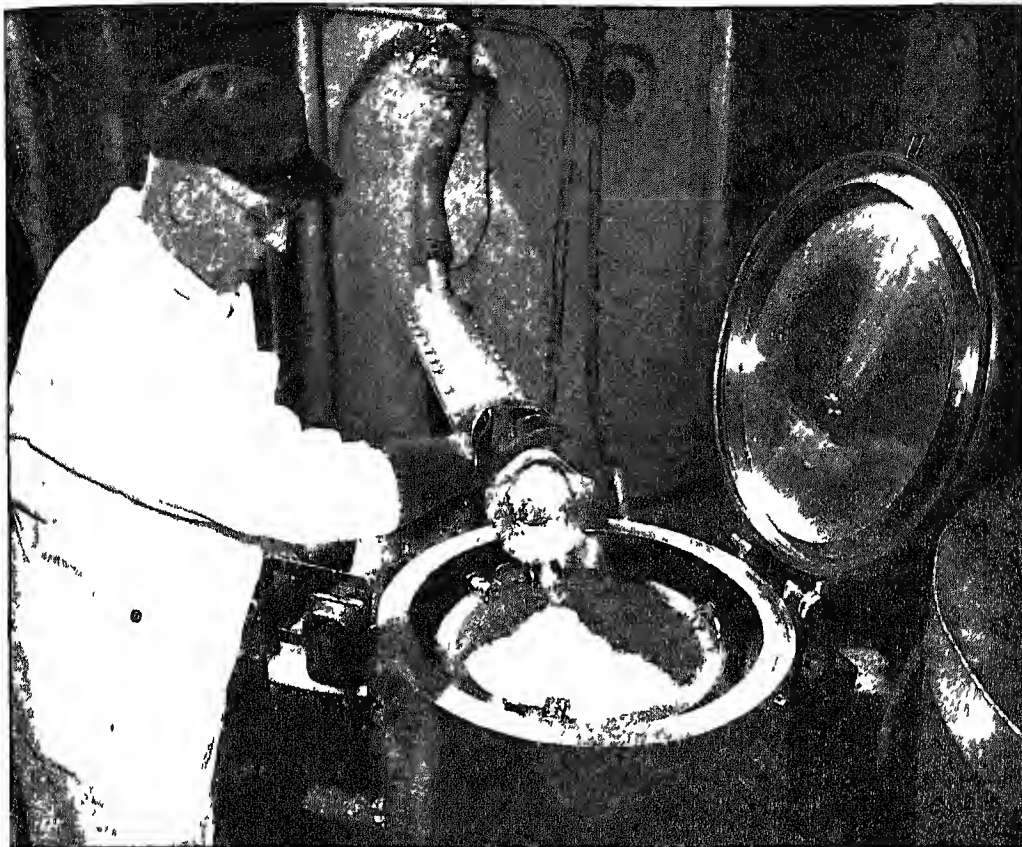


Figure 93. Production of Silver Nitrate

Silver nitrate is produced by crystallization of "silver salt" from a solution of silver in nitric acid. A new method is now used to replace the old way of making the crystals by evaporation in open porcelain dishes.

to about 12 or 13 g. at 0° , whereas the solubilities of the other substances (NaCl , KCl , and NaNO_3) do not vary nearly as much. Hence, the first batch of crystals that forms, as the temperature drops, will consist principally of potassium nitrate. If these are dissolved in water, and the solution is again evaporated, filtered, and cooled, the first crystals that form upon cooling will again consist largely of potassium nitrate and will be more nearly pure than those first obtained. By repetition of this process practically pure potassium nitrate can be prepared. This process is called *fractional crystallization*, it is often used in purifying substances that are readily crystallized from solutions. For the purification of organic compounds, alcohol

or ether may be substituted for water, if the compounds are more readily soluble in these solvents.

13 Diffusion in Solution

The fact that solutions are homogeneous mixtures must mean that the molecules of the solute, however few of these there may be in a definite volume of the solution, separate from one another and become uniformly distributed throughout the mixture. If a few crystals of a highly colored substance, such as potassium permanganate, are placed in the bottom of a cylinder that is filled with water, the substance passes into solution. After some time, the color of the solution becomes uniform from top to bottom, and we

can say that the mixture is homogeneous. The particles of the solute that appear in the upper portion of the solution arrive there by diffusion, provided that the solution is not disturbed by stirring or shaking. In this respect the molecules of the solute act in the same manner as gas molecules. There are many more molecules in a solution, however, than in an equal volume of a gas, in which the molecules are far apart. This condition results in a greater number of collisions in solution and decreases the rate at which molecules of one substance can penetrate the space occupied by another. The process is further retarded by the slower velocities of molecules in the liquid state. Unless aided by stirring or some form of agitation, a very long time — measured for most solutions in days instead of minutes — is required for diffusion to produce a homogeneous mixture.

14. Distribution of a Solute Between Two Immiscible Solvents

What happens when two solvents compete for the same solute? This situation is sometimes encountered in the laboratory. In one of the tests used to detect the presence of iodide ion, I^- , in aqueous solutions, the iodide is first oxidized to free iodine, I_2 , which dissolves slightly in water. A few drops of an organic liquid, such as carbon disulfide, CS_2 , which is immiscible with water are added, and the mixture is shaken. The iodine is more soluble in carbon disulfide than in water. A large part of it, therefore, leaves the solution in water and dissolves in the organic liquid, which is lighter than water, and hence the organic liquid separates as the top layer. This solution is more concentrated than the original aqueous solution and reveals more clearly the presence of iodine, which forms in carbon disulfide a pink to violet solution, depending upon the concentration. By this process iodine is extracted from an aqueous solution. By similar procedure many substances useful in medicine are extracted with alcohol or some

other liquid from the natural materials in which they are found.

A solute is distributed between two immiscible solvents in proportion to the solubility of the substance in each of the solvents. This is called the Distribution Law, and the ratio of the solubilities of the solute in the two solvents is called the *Distribution Ratio*. The value of this ratio is constant for a definite temperature, provided that the composition of the molecules of solute in the two solutions is the same.

15. Evidence of Chemical Changes in Solutions

Although solutions are to be regarded as simple mixtures of the particles — molecules or ions — of two or more substances, there are indications of chemical changes when many solutions are made. Such changes often determine, in large measure, the extent to which one substance dissolves in another. In some solutions the evidence of chemical change is slight, and the solutions behave almost as simple mixtures, a solution of this kind approaches in behavior the conditions that we should expect in an *ideal solution*.

Some of the evidence that indicates chemical changes when certain solutions are made is summarized below.

(1) *Volume Changes* The volume of a solution containing two substances might be expected to equal the sum of the volumes of the components before they are mixed. In many cases, however, the volume of the solution is greater or less than this sum. If 500 ml of alcohol is mixed with 500 ml of water, for example, the volume of the mixture is about 965 ml instead of 1000 ml. Such changes in volume may in some instances be produced by reactions between solute and solvent which result in a change in the total number of molecules as well as in the kind of molecules in the mixture. In other solutions the change may result from the relatively strong forces of attraction between molecules of solute and solvent, forces which bind the molecules of the two substances more closely together than the molecules of either substance alone are held.

(2) *Temperature Changes* When solutions are made, some temperature change is to be expected

in all cases involving two substances of different physical states. The mixing of two gases or two liquids need not involve the absorption or liberation of energy, if the solution resulting is a simple mixture. But when a gas dissolves in a liquid, we must think of the solute as having been converted from the gaseous to the liquid state, a change which involves energy. If a solid dissolves in a liquid, we must think of the solid as having been changed to a liquid. This change also involves energy. In the solution of a gas the change of state to the liquid should mean that heat is liberated. For solids heat should be absorbed. We might expect, therefore, that the solution of a gas in a liquid should result in an increase in temperature. If we were to supply heat we should expect the change to occur in the opposite direction. This is undoubtedly one condition which causes the solubility of all gases to decrease with rising temperature. On the other hand, the solution of a solid in a liquid should result in decreased temperatures, and solubility might be expected to increase as the temperature rises. This is generally but not always true (page 197).

If changes of state were the only causes of temperature changes in the formation of solutions, we should expect that the changes occurring could be predicted with a fair degree of accuracy. Usually, however, this is not the case. It often happens, for example, that the solution of a solid in a liquid results in the liberation of heat. Thus, the solution of one gram-molecular weight of ammonium nitrate in 200 gram-molecular weights of water (about 3600 ml.) results in the absorption of 6320 calories, while the solution of one gram-molecular weight of sodium hydroxide in the same quantity of water results in the liberation of 9940 calories. The solution of one gram-molecular weight of calcium chloride in 300 gram-molecular weights of water liberates 17,410 calories. A solution in which ammonium nitrate is dissolved becomes colder, while solutions of sodium hydroxide and calcium chloride become warmer. Water placed beneath a beaker in which ammonium nitrate is dissolving can be frozen, while water into which sulfuric acid is poured can be made to boil.

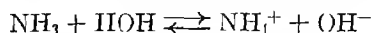
Whenever abnormal heat changes occur, as solutions are made, we can be reasonably certain that chemical change is going on. In a solution of calcium chloride in water, for example, the change probably involves the formation of the

hydrate $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ from the anhydrous salt. When the hydrate dissolves, we find that heat is absorbed and that the temperature falls, if one gram-molecular weight of $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ is dissolved in 100 gram-molecular weights of water, 4310 calories of heat are absorbed. The difference between the heat change in this solution and that in the solution of the anhydrous salt is clearly due to a chemical change which occurs in the latter but not in the former.

16 Evidence of Definite Compound Formation in Solution

When many substances are dissolved and the resulting solutions are evaporated, the crystals produced are not those of the substance originally dissolved but of a hydrate (page 181). Thus, from solutions of sodium sulfate we obtain crystals (below 32°) of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, and from solutions of cupric sulfate, crystals of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. The formation of these substances is definite evidence of chemical change, and the most logical assumption is that the change occurred when the substances were dissolved. We cannot argue, of course, that the extent to which water is combined with the ions of a salt is the same in the solution as it is in the crystalline state; it may be the same, it may be more, or it may be less. We have no convenient way of determining the answer to this question.

Still more direct evidence of chemical change is obtained when a compound is formed which has no existence outside the solution. Thus, neither water nor ammonia has any effect on litmus paper. But when ammonia dissolves in water, the solution turns red litmus blue. This behavior indicates that the solution contains hydroxyl ions. Accordingly, we must conclude that ammonia reacts, at least to some extent, with water to form ammonium and hydroxyl ions. A solution containing these ions is usually called ammonium hydroxide.



Similarly, we must conclude that solutions of the oxides of non-metals such as carbon

dioxide, sulfur dioxide, and phosphorus pentoxide contain acids, which are produced by the reaction of the oxides with water. A solution made by mixing calcium oxide and water contains calcium hydroxide. When sodium peroxide appears to dissolve, it actually reacts with water to form oxygen and sodium hydroxide, and the latter forms the solute of the solution. The extent to which reactions of this kind occur is an important factor in determining the quantity of the substance that dissolves in a definite volume of the solvent. We must assume that the quantity of sulfur dioxide, for example, that dissolves in a liter of water would be considerably different, if the solute did not react with water to form sulfurous acid.

THE CONCENTRATION OF SOLUTIONS

17 Comparisons of Solutions

It is often necessary to compare one solution with another with respect to the relative amounts of solute and solvent that they contain. Frequently, also, solutions containing definite weights of a solute per volume must be prepared for use in the laboratory, in medicine, or elsewhere. A rough comparison can be made by classifying one solution as concentrated and another as dilute, depending upon the relative amounts of solute that they contain in the same volume of solution, but this distinction is indefinite and gives, of course, no exact information about the composition of the solutions. A solution that is concentrated as compared to another may be dilute as compared to a third.

The concentration of a solution represents the quantity of solute in a definite quantity of the solution or of pure solvent. To express concentration in a uniform manner—a condition that is necessary when comparisons are to be made—suitable units must be adopted. One system expresses the weight in grams of the solute in 100 ml of the solution, in 100 ml of the pure solvent, or in 100 g of the solvent. If expressed as grams of solute per 100 g of solvent, the concentra-

tion can also be stated in percentage. The concentration is usually expressed, however, in terms of *molar*, *normal*, or *molal* solutions. These terms are explained in the sections that follow.

18. Molar Solution

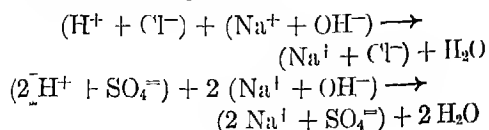
Many of the physical properties of a solution, such as the freezing point, depend upon the *number of molecules* of solute in a definite volume of solution—more exactly, in a definite quantity of pure solvent; hence it is frequently desirable to express concentration in terms of gram-molecular weights, instead of grams, of solute.

A solution containing one gram-molecular weight of a solute in one liter of solution is called a *molar solution*¹. It is evident, of course, that a solution containing two gram-molecular weights in two liters has the same concentration as a solution containing one gram-molecular weight in one liter or one-tenth of a gram-molecular weight in one-tenth of a liter. A solution of which one liter contains two gram-molecular weights of solute is a two molar (2 M) solution, and one containing one-tenth of a gram-molecular weight in one liter is a one-tenth molar (0.1 M) solution.

To prepare a molar solution of sulfuric acid we mix 98.076 g of the acid with sufficient water to form one liter of solution. A molar solution of sodium hydroxide contains 40.008 g of the solute per liter, and a solution of hydrochloric acid contains 36.468 g of acid per liter. If molar solutions of hydrochloric acid and sulfuric acid are added to equal volumes of a molar solution of sodium hydroxide, the volume of the solution of the acid required for complete neutralization of the base will be found to be twice as great for hydrochloric acid as for sulfuric acid. This difference depends upon the fact that one gram-molecular weight of sulfuric acid reacts with two gram-molecular weights of

¹ For ionic compounds, such as sodium hydroxide, the gram-molecular weight is really the gram-formula weight (page 140).

sodium hydroxide, while one gram-molecular weight of hydrochloric acid reacts with only one of sodium hydroxide



19. Normal Solution

In exact comparisons of one solution with another, the concentrations should be defined in such a manner that equal volumes of the solutions of the same concentration are actually equivalent. This is not true of molar solutions, because one liter of molar sulfuric acid, as shown above, is equivalent to two liters of molar hydrochloric acid in the reaction with sodium hydroxide. If concentration is expressed as the number of *equivalent weights* of solute per liter of solution, equal volumes of solutions of different substances will react with the same volume of the solution of a third substance.

A solution containing one gram-equivalent weight of solute per liter is a normal solution. According to this method of designating the concentration, solutions are described as N, 2N, 10N, 0.1N, or N/10, etc., depending upon the number of gram-equivalent weights, or fraction thereof, per liter. These symbols represent the *normality* of the solution.

The equivalent weight of hydrochloric acid is the same as the molecular weight, since each molecule contains one atom of hydrogen, a normal solution of hydrochloric acid contains the same weight of acid per liter as a molar solution. A molecule of sulfuric acid, however, contains two hydrogen atoms, and the equivalent weight is consequently one half of the molecular weight, hence a molar solution of this substance contains twice as much acid as an equal volume of the normal solution. Two liters, one of normal hydrochloric and the other of normal sulfuric acid, contain the same quantities of hydrogen, and each will neutralize one liter of normal sodium hydroxide. One liter of normal phosphoric acid (H_3PO_4) solution contains one third of a molecular weight. Table 7 shows the weights of other substances in one liter of their normal solutions and also the *normality* and molar concentration of solutions containing other weights of the solutes.

A 1 N solution of any hydroxide contains 17.008 g. of hydroxyl ion, or the equivalent weight of the hydroxide, per liter, one OH^- ion is equivalent to one H^+ ion. To find the weight of a salt required to make one liter of a 1 N solution, divide the formula weight by the total of *either* the positive or the negative charges on the ions of the salt. Thus, for Na_2SO_4 one-half of the gram-molecular, or gram-formula, weight would be required to make one liter of 1 N solution.

The normality of a solution of unknown con-

TABLE 7

The Normality of Solutions

Substance	Mol. Wt.	Weight per Liter of 1 N Solution	If the Weight per Liter Is	The Normality is	The Molar Concentration is
Barium hydroxide ($\text{Ba}(\text{OH})_2$)	171.39	85.695	21.424	0.25 N or $\frac{N}{4}$	1/8 M
Sodium sulfate (Na_2SO_4)	142.064	71.032	7.103	0.1 N or $\frac{N}{10}$	1/20 M
Sodium chloride (NaCl)	58.46	58.46	29.23	0.5 N or $\frac{N}{2}$	1/2 M
Stannic chloride (SnCl_4)	260.54	65.135	0.6514	0.01 N or $\frac{N}{100}$	1/400 M

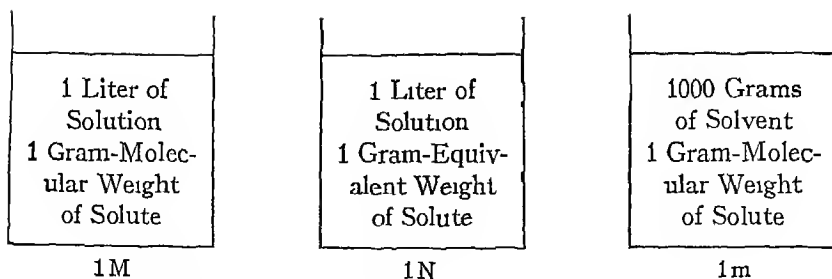


Figure 94 Comparison of 1 Molar, 1 Normal, and 1 Molal Solutions

centration can be determined if the volume of a solution of known normality with which a definite volume of the "unknown" reacts is found by experiment. If the concentration of the solution of known normality is 1 N, and equal volumes of the two solutions react, then the normality of the "unknown" is also 1, but if only half as much of the "unknown" is required, its concentration is 2 N, and so on.

20. Molal Solution

Concentration is also expressed as the number of gram-molecular weights, or the fraction of a gram-molecular weight, of the solute dissolved in 1000 g of solvent. A solution containing 1 gram-molecular weight of solute in 1000 g of solvent is said to have a concentration of one *molal* (1 m). For very dilute solutions the molal and the molar concentrations are practically identical, but in concentrated solutions there may be considerable difference between the two.

21. Sample Problem Involving Concentration

If 200 ml. of a solution containing 4 g of sodium hydroxide per liter is required to neutralize completely 100 ml of a solution of sulfuric acid, what is the normality of the solution of the acid?

A normal solution of sodium hydroxide contains 40 g of the base per liter. Hence a solution containing 4 g per liter contains only 1/10 as much sodium hydroxide and its concentration is 0.1 N. Now if 100 ml. of the solution of the acid neutralizes 200 ml. of the base, 1 liter of the acid's solution will neutralize 2 liters of the base. Hence the concentration of the acid must be twice as great as that of the base, or 0.2 N.

22. Equilibrium Between a Solution and the Undissolved Solute

(1) *Gas Dissolved in a Liquid* Let us consider a solution of carbon dioxide in water. In a closed vessel containing water in the lower part and carbon dioxide in the space above the liquid, molecules of the gas that strike the surface may penetrate the body of the liquid, thereby forming a solution. These molecules may also leave the solution if, upon coming to the surface from below, they possess sufficient energy to break away from the attraction that binds them to water molecules. After a time, when molecules of the gas enter and leave the solution at the same rate, a state of equilibrium resembling the equilibrium between a liquid and its vapor will be established. This equilibrium may be disturbed by changes in the temperature or by changes in the pressure of carbon dioxide above the liquid. If, for example, the pressure of the gas is increased by forcing more of it into this space, more molecules strike the surface and enter the liquid than leave the liquid in the same period of time; and hence the solution becomes more concentrated. When equilibrium is established again, the solution will contain a greater quantity of the gas per liter, and there also will be present above the liquid more of the undissolved gas per unit of volume. In general, the solubility of a gas in a liquid follows Henry's law (page 194).

If the temperature of a solution of a gas in a liquid is raised, equilibrium between the solution and the undissolved gas above the solution is disturbed, because molecules

of the gas leave the solution in greater numbers than they enter it. The concentration of such a solution decreases with rise in temperature, in an open vessel in which there can be no appreciable pressure of the gas above the surface of the liquid, the dissolved gas can be expelled completely from the solution by heating. The same result would be produced eventually at room temperature, but it is considerably hastened by heating.

In the boiling liquid the removal of the gas is still further accelerated, because it escapes into every bubble of water vapor that forms in the solution, and thus is carried away. The dissolved gas may also be removed by bubbling another gas — air is often used, and sometimes nitrogen because it is inactive — through the solution. Every bubble that leaves the solution carries with it some of the dissolved gas, which escapes into the bubble for the same reason that it escapes into the space above the surface of its solution; bubbles simply increase the amount of surface.

The *solubility of a gas* in a liquid refers to the quantity that dissolves in a definite volume, or weight, of a liquid at a definite temperature and under a definite partial pressure of the gas. The partial pressure is usually 760 mm, the quantity of gas may be expressed as grams or as the number of milliliters (ml); the quantity of liquid solvent is usually 100 ml or 100 g. The solubility of gases may be expressed, also, as the number of gram-molecular weights per liter of solution.

(2) *A Solid Dissolved in a Liquid.* A solid or a liquid also reaches a state of equilibrium with its solution, if it is added in excess of the quantity that dissolves. Let us consider the solution of a solid in a liquid (Figure 95). Molecules — or ions, if the substance is composed of ions — enter the solution from the surface of the solid, for sodium chloride the particles that enter the solution are sodium and chloride ions, while for sugar they are molecules. As they move through the solution, some of the particles of the solute may

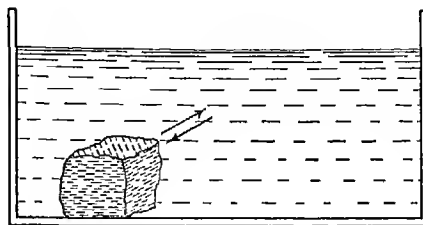


Figure 95 The Conditions Required for Saturation
The Equilibrium Between the Solution and Undissolved
Sodium Chloride

come into contact with the surface of the solid, and of these a certain number will be caught and held by the same forces that originally held them in the crystal. The number of particles thus returning to the crystal's structure, out of the total number that strike the surface, depends upon several factors, among which are (1) the strength of the attraction that binds the particles in the crystal, and (2) the kinetic energy of the particles, a condition that depends upon the temperature of the solution. Equilibrium between the solid and its solution is reached when particles enter the solution and return to the solid at the same rate. Equilibrium of the entire volume of the solution with the solute is obtained more quickly by stirring or shaking, because the rate of diffusion of the solute is slow. Agitation therefore increases the rate of solution.

23. Saturated Solutions

The state of equilibrium between the undissolved portion of a substance and its solution requires that the solute be present in both conditions, dissolved and undissolved. Under these conditions we can say that the solution contains as much of the solute per unit of volume as it can hold. A *saturated* solution is defined as one in equilibrium with the undissolved solute.

We cannot be certain that a solution is saturated in the absence of the undissolved solute. When equilibrium has been established the saturated solution can be separated from the excess of the solute by decantation or filtration, but when this is done we cannot be certain that the solution remains satu-

rated, unless we know that the conditions remain absolutely constant. There must be no change in temperature, for example, and none of the solvent should be allowed to evaporate. The quantity of solute per unit volume of a saturated solution is called the *solubility* of the solute and is expressed, usually, as grams per 100 ml. or per 100 g. of solution or as gram-molecular weights per liter.

The solubility of most solids increases with the temperature. This means that more particles must be present, per unit volume of the solution in contact with the solid, to establish equilibrium as the temperature increases. This requirement is due, no doubt, to the greater kinetic energy of the particles at the higher temperature. The greater the energy, the smaller the percentage of the particles striking the surface that re-enter the solid state.

24. Supersaturated Solutions

If a solution that is saturated with a solid solute at a moderately high temperature is separated from the excess of solute and cooled to a lower temperature, usually it will contain more of the solute per unit of volume than corresponds to the solubility of the solute at the lower temperature. We should expect the excess of the solute to separate as crystals from the solution as the temperature falls, but in the absence of at least a small quantity of the solid, separation may not occur. The condition of the solution is then described as *supersaturated*.

Supersaturation is not difficult to understand, when we take into consideration the character of the solid state. As previously shown, particles of most solids are arranged in regular patterns (compare the crystal structure of sodium chloride, page 56). Now if a structure such as this is in contact with a solution, particles of the solute that come into contact with its surface may join the structure already existing (Figure 96), but if the solution is in contact with no such structure, then a certain number of particles

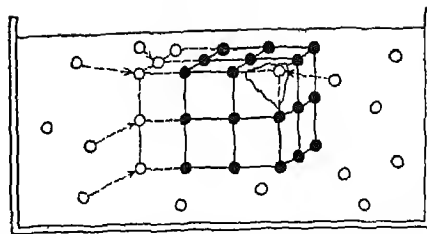


Figure 96 Supersaturation is impossible in the Presence of the Undissolved Solute

Sodium and chloride ions in this solution of sodium chloride may join the ions composing the crystal that already exists, thus causing the crystal to grow and making a supersaturated solution impossible.

must simultaneously come into the required positions to establish the first unit of crystalline growth. Equilibrium as applied to a solution is defined as the condition resulting when particles of the solute leave the solid state and *return to it* at the same rate. If the solid state is not present, there is nothing to which the particles can return from the solution. Until a portion of the solid structure is begun, it is evident, therefore, that the solution may contain a greater concentration of the solute than corresponds to the actual solubility. The addition of a very small crystal of the solute starts crystallization and relieves the supersaturation. Adding other kinds of crystals, shaking the solution, and scratching the inner wall of a glass vessel containing the solution are other methods sometimes used to start the separation of the solid. A scratch may leave an irregular array of molecules which attract molecules of the solute from the solution in the same manner that crystals of the solute itself attract them.

Our explanation of supersaturation does not cover all cases. It does not show, for example, why some substances form supersaturated solutions more readily than others, or why some supersaturated solutions are reduced to the saturated state more easily than others. Nor does it explain the formation of supersaturated solutions of gases, for which supersaturation is more often encountered than for any other type of solute. Soda water, ginger ale, and other carbonated waters are often supersaturated, even after they

have been poured into open vessels. Carbon dioxide first escapes in large quantities, but the ebullition soon ceases. It may be started again, however, if the solution is stirred or shaken.

THE PROPERTIES OF SOLUTIONS

25. Introduction

The properties of solutions to which we refer in this section are physical in character and include *vapor pressure, boiling point, freezing point, and osmotic pressure*. There is a high degree of regularity in the properties of solutions containing different solutes in the same solvent. The important factor in the determination of the exact values of these properties appears to be the *number of particles* of the solute that is mixed with a definite number of molecules of a given solvent. Usually, the weight of the solvent is fixed as 1000 g. In 1000 g. of water, for example, there are $1000/18 = 55.5$ gram-molecular weights. Now, if one gram-molecular weight of any solute is dissolved in this weight of water, we find that the properties of the solution are the same, regardless of the nature of the solute, *provided no change occurs except that resulting in a mixture of the two kinds of molecules*. If a change occurs, producing fewer or more particles than are contained in 55.5 gram-molecular weights of water and one gram-molecular weight of the solute, the properties of the solution will vary, of course, to an extent depending upon the extent of this change.

In speaking of solutions in this section we shall refer to mixtures of solids and liquids unless otherwise stated. We shall assume that the solid solute has a negligible vapor pressure as compared with the solvent. Although we shall usually speak of water as the solvent, our statements can be applied to solutions in other solvents, provided that proper changes are made in the numerical values quoted. These changes will be indicated as they appear in the discussion that follows.

The regularities to which we shall refer in dealing with the properties of solutions are subject to certain restrictions. They are exact only for dilute or, at the most, moderately concentrated solutions, and they hold true only for solutes which are non-electrolytes. Even for many substances which are not recognized as electrolytes the laws fail to hold exactly. For salts, acids, and bases they often fail completely, but even for some of these substances the relations are at least qualitatively valid. The deviations of the properties of solutions of electrolytes from the regularities displayed by solutions of non-electrolytes will be discussed in a later chapter. These deviations are of great significance. They arise from the fact that ionic compounds, or other compounds that produce ions in solution, liberate more particles than correspond to the number of particles in a gram-molecular weight of a compound composed of molecules. A gram-molecular (or formula) weight of Na^+Cl^- , for example, produces in a solution twice as many particles (Na^+ and Cl^- ions) as it would if it were made up of NaCl molecules, each ion has as much effect upon the properties of the solution as a molecule.

26. Vapor Pressure

Although we sometimes speak of the "vapor pressure of a solution," we refer usually only to the vapor pressure of the water (or other solvent). Since a solution is not a chemical compound, it cannot have a characteristic vapor pressure of its own, and since water is not chemically changed when it becomes a part of a solution, we must expect water molecules in a solution to behave as they do in the pure solvent, subject of course to certain physical conditions resulting from the presence of the solute. Thus, the water molecules in a solution escape through the surface to produce water vapor, and an equilibrium is set up between the vapor and the water in the solution. At a given temperature, however, the pressure of the vapor at equilibrium is always less than the pressure of the vapor in equilibrium with the pure liquid. We assume here that the solute has only a negligible vapor pressure. In dealing with solid solutes this assumption is almost always justified.

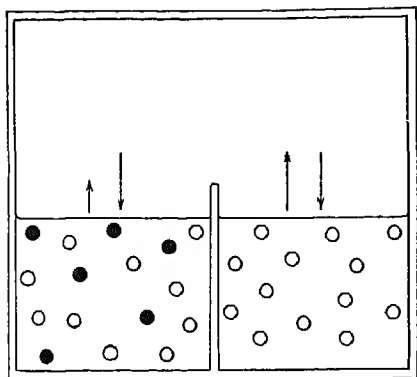


Figure 97 The Vapor Pressures of a Solution (left) and Pure Solvent (right)

Why is the tendency of water to evaporate from a solution less than the tendency of pure water to evaporate? Let us consider a solution of sugar in water. The water molecules that strike the surface probably have almost as much chance of escaping as do those of the pure solvent, if the solution is dilute. It is true, of course, that the chance will not be as great, if the attraction between molecules of water and sugar is strong — stronger than the attraction of water molecules for one another, this attraction, however, does not affect the behavior of water molecules to an appreciable extent until the concentration of sugar becomes fairly high. But to the extent that it does have an effect, it will lower the vapor pressure of the water.

Since, however, the effect of a solute upon the vapor pressure of a solvent in dilute solutions is practically independent of the nature of the solute, as long as no chemical change occurs when the solution is formed, it would appear that attraction between molecules of solute and solvent is not the only important factor determining the extent to which the vapor pressure of the solvent is decreased. Probably of greater significance, in dilute solutions, is the simple effect of sugar molecules in impeding the motion of water molecules, thus decreasing the number that reach the surface in a certain period of time. The sugar molecules do not escape

through the surface to form vapor, they act, therefore, as obstacles in the path of water molecules. If this is a primary cause of the decrease in the vapor pressure of water, the kind of solute molecule has little to do in determining the extent of the effect, and furthermore, the decrease in vapor pressure should be proportional to the number of molecules of solute that is mixed with a definite number of molecules of solvent.

27 Raoult's Law

Raoult formulated a law, now called by his name, which deals with the relation of the concentration of the solute to the lowering of the vapor pressure of the solvent. This law is stated as follows: *The lowering of the vapor pressure of a solvent by a solute is directly proportional to the weight of that solute dissolved in a definite weight of the solvent.* This law holds true only for dilute solutions, and only if the solute and solvent do not react. Raoult's law is also stated sometimes as follows: The vapor pressure of the solvent in a solution is directly proportional to the *mole fraction* of that substance in the solution. The mole fraction of the solvent refers to the fraction (of the whole number of molecules present in the solution) that consists of solvent molecules. Thus, the mole fraction of water molecules in a molal sugar solution (1 g.-mol wt of sugar per 1000 g. of water) is $55.5/55.5 + 1 = 0.983$. The vapor pressure of the water in this solution is, consequently, only 0.983 of the vapor pressure of pure water.

In studying the effect of solutes upon the properties of the solvent, or more often in studying the condition of the solute in the solution, vapor pressure determinations are seldom employed, because of the difficulties involved in their measurement. Instead, boiling and freezing points are determined, but since these properties are dependent upon vapor pressure, the results measure the same effects.

28 The Lowering of the Freezing Point of the Solvent

When an unsaturated solution is cooled to a sufficiently low temperature, the crystals produced as the result of freezing are those of the pure solvent, not of the solution itself. The temperature at which these crystals are formed is below the freezing point of the pure solvent. Thus, sea water freezes at a lower temperature than fresh water because the former contains larger quantities of substances in solution. We use aqueous solutions of various substances (glycerine, glycol, alcohol) instead of pure water in automobile radiators because they freeze at lower temperatures. The water of the car's storage battery does not freeze, during winter weather, because it contains sulfuric acid in solution.

Let us consider the freezing point of pure water and of the water in a sugar solution. Refer to Figure 98. It will be seen that pure water and ice have the same vapor pressure at 0°C , but this is not true of ice and the water in a solution. At 0°C , the vapor pressure of ice is greater than that of the water in the solution, hence, if the two were placed together, the ice would melt and the solution would become more dilute. At a temperature somewhat lower than 0° , the vapor pressure of water in the solution is the same as that of ice, and at this temperature the solution and ice are in equilibrium. This temperature corresponds to the point of intersection of the two curves, one representing the vapor pressure of ice and the other the aqueous vapor pressure of the solution.

29. Freezing Mixtures

A mixture of a solvent and a substance dissolved in it has a lower freezing point than the pure solvent. If salt, for example, is mixed with ice, a temperature lower than the melting point (0°C) of ice can be secured. As ice melts, salt dissolves in the water, forming a solution which has a lower vapor pressure than water or ice, hence solutions and ice are not in equilibrium. The ice consequently melts, and since this process requires

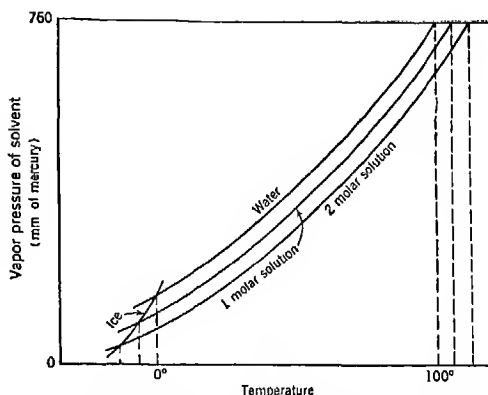


Figure 98 The Effect of a Solute upon the Vapor Pressure of a Solvent (water)

about 80 calories of heat for each gram of ice that changes to liquid, the mixture undergoes a decrease in temperature.

This withdrawal of heat may be employed to freeze a liquid in a vessel which is immersed in the bath of ice, salt, and water. For this reason, a salt and ice mixture is used to freeze and to pack ice cream. On the same principle, it is possible to clean icy streets and sidewalks by strewing salt upon the ice.

The lowest temperature attainable in any mixture of ice, water, and soluble solid (such as salt) is the eutectic temperature (page 210). The more soluble the solute, the lower is this temperature, which is determined largely by the quantity of solute required to saturate a definite volume of solvent. Thus, for potassium nitrate, the eutectic temperature is only three degrees below zero, for sodium chloride it is -22.4° , and for calcium chloride it is -55° .

30 Elevation of the Boiling Point of the Solvent

Since the boiling point is defined as the temperature at which the vapor pressure of the liquid becomes equal to the atmospheric pressure, it is evident that any change in either the atmospheric pressure or in the vapor pressure of the liquid will cause a corresponding change in the boiling point. We have already noted (page 208) that the vapor pressure of a liquid solvent is lowered by the presence of a solute. Hence a solution must be raised to a higher temperature

than the pure solvent before the vapor pressure becomes equal to a constant atmospheric pressure. This condition may be easily understood by inspecting Figure 98.

As explained on page 208, the lowering of the vapor pressure of the solvent by a solute is directly proportional to the weight of the solute which is mixed with a definite weight of the solvent. Since the boiling point is elevated to an extent which is proportional to the lowering of the vapor pressure of the solvent, we can also conclude that the *elevation* of the boiling point is also proportional to the weight of the solute dissolved in a definite weight of the solvent. Since the lowering of the vapor pressure is independent of the nature of the solute, with the exceptions previously noted (page 208), we can also conclude that the boiling point is raised the same amount by equal numbers of molecular weights, or equal fractions of the molecular weights, of different solutes. This means, for example, that one gram-molecular weight of sucrose ($C_{12}H_{22}O_{11}$) and one gram-molecular weight of glucose ($C_6H_{12}O_6$), in 1000 g of water, form solutions which have the same boiling points. The vapor pressures and the freezing points of these two solutions are also the same.

Furthermore, a solution containing one gram-molecular weight of any non-electrolyte as solute in 1000 g of water has the same vapor pressure, boiling point, and freezing points as the sucrose and glucose solutions. This statement may be considered as a corollary of Raoult's law (page 208).

31 Eutectic Mixtures

As the pure solvent freezes out of a solution, the concentration of the solute must become greater. The increase in concentration leads, of course, to a lower freezing temperature. The solution may eventually become saturated with the solute, and when this happens, both solvent and solute will crystallize upon further cooling, and the concentration of the solution will remain constant. A solution that acts in this manner

is called a *eutectic* mixture, and the eutectic temperature may be defined as the temperature at which both solvent and solute separate as solids from the mixture. This temperature is the lowest freezing point of the solution.

32 Osmosis

Osmosis refers to the unequal rates of transfer of a liquid in two directions through a membrane. To demonstrate it we must separate a pure liquid from a solution in which the liquid acts as the solvent, or we may separate a dilute solution from a more concentrated solution of the same solvent. The separating wall must consist of a membrane that is permeable to the solvent but impermeable to the solute. Different animal and vegetable membranes act in this manner, parchment and cellophane that has not been waterproofed are often used, and when a stronger wall is desired, copper ferrocyanide is deposited in the pores of an unglazed clay flask or tube.

Figure 99 shows a convenient method of

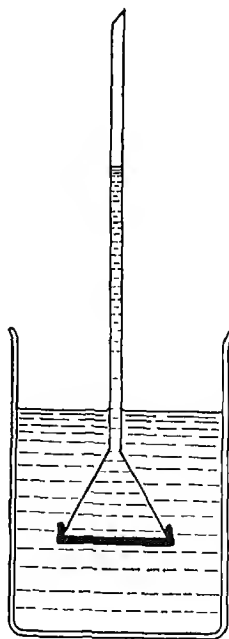


Figure 99 Diagram of Apparatus Used to Demonstrate Osmosis

demonstrating osmosis. A sheet of parchment paper is fastened tightly over the larger end of a funnel or thistle tube, into which a moderately concentrated solution of sucrose, for example, is placed. The inverted funnel or thistle tube is then immersed in pure water. Water flows through the membrane into the solution and the latter rises in the tube.

The transfer of molecules through a membrane is not a simple case of diffusion through tiny openings. Without attempting an explanation of how water molecules pass through the membrane and why molecules of the solute do not, let us consider the rate of transfer of water molecules in the two directions (Figure 100). The rates at which water molecules pass through the membrane are not equal, for all of the molecules on one side of the membrane are water molecules, while some of the molecules on the other side are sugar molecules. The difference in the rates depends upon the percentage of molecules of sugar in the solution. The water, therefore, continues to pass through the membrane into the solution, and the column of the solution (in the tube as shown in Figure 99) continues to rise, until the hydrostatic pressure becomes equal to what is commonly called the osmotic pressure of the solution, a pressure that depends upon the unequal concentrations of water on the two sides of the membrane.

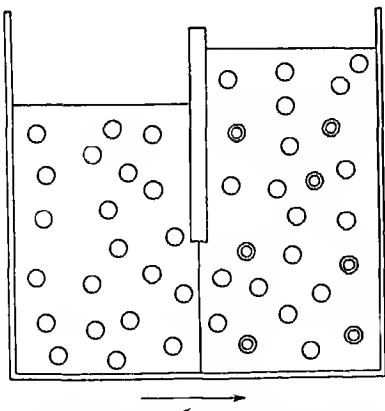


Figure 100 An Explanation of Osmosis
The solution is on the right-hand side

33. Osmotic Pressure

We shall understand more clearly the meaning of the term *osmotic pressure* if we approach the subject by considering the difference between the pure liquid and its solution as shown by their vapor pressures. If two beakers, one containing a pure liquid (let us use water) and the other a solution in which the same liquid is the solvent, are placed in the same closed atmosphere (under a bell-jar, for example), the two will be found not to be in equilibrium. As we have shown previously, the vapor pressure of water in the solution is lower than that of pure water, hence the equilibrium between water and vapor requires a greater vapor pressure than the equilibrium of solution and vapor. Water, therefore, can and will place a greater quantity of water vapor in the atmosphere of the container than the solution. This excess of vapor condenses to dilute the solution, because molecules of water enter the solution more rapidly than they leave it. The vapor pressure in the space above the liquids is thus reduced, disturbing the equilibrium between pure water and vapor; as a result, more of the pure liquid evaporates. At a constant temperature, therefore, equilibrium between a pure liquid and its solution cannot be established because of the difference in the evaporating or escaping tendencies of the water molecules in the two conditions.

For the conditions discussed in the preceding paragraph the atmosphere above them provides the separating medium between pure liquid and solution. If we place a semi-permeable membrane between them, the effect is much the same. Water molecules escape by passing through the membrane in both directions, but as before there is a difference in escaping tendencies due to the presence of the solute on one side and its absence on the other. It is possible to equalize the escaping tendencies of water molecules on the two sides of the membrane by increasing the pressure upon the solution. An increase in the pressure causes molecules to leave the solution and pass through the

membrane into the pure water at a faster rate. For example, the pressure produced by the solution as it rises in the tube of the apparatus used to demonstrate osmosis (Figure 99) represents an increase in the pressure exerted upon the solution. As the column of liquid rises, the pressure upon the solution increases. When the solution ceases to rise in the tube, the pressure has increased sufficiently to cause the water molecules on the solution side to escape through the membrane at the same rate as water molecules escape on the pure water side. The pressure required to equalize the escaping tendencies of water molecules on the two sides of the membrane is equal to the osmotic pressure. Instead of measuring the height of the column of solution that exerts a pressure equal to the osmotic pressure, it is often more convenient to measure the same pressure by impressing upon the solution a pressure which will stop osmosis and which can easily be measured. A device by which such pressure can be applied is shown in Figure 101.

The osmotic pressure of a solution containing one gram-molecular weight of a solute (a

non-electrolyte) dissolved in 1000 g of water is 22.4 atmospheres at 0° when the membrane is perfectly semipermeable, i.e., it allows no molecules of solute to pass through it. As the temperature rises, the osmotic pressure increases. At room temperature the osmotic pressure of the solution described above is about 24 atmospheres.

If two solutions of unequal concentration are separated by a semipermeable membrane, the solvent passes from the more dilute to the more concentrated solution. Two solutions which have the same osmotic pressure are said to be *isotonic*. Thus, the blood and the solution inside the corpuscles are isotonic. If they were not, the effect would be disastrous. If the blood were replaced by water, for example, the passage of this substance through the walls of the corpuscles would produce sufficient pressure to burst these bodies, whereas if the solution inside them were more dilute, water would pass out of them into the blood, and the corpuscles would shrink in size. The same effect would be produced if the blood were made more concentrated by the injection of solutions of salts or other substances.

Osmosis must play an important part in the absorption by plants of water from the soil. Water passes through the walls of the plant's roots because the solution inside is more concentrated. This does not mean, however, that the rise of sap to the top of the plant is caused solely by osmotic pressure. Other conditions play important parts in this action.

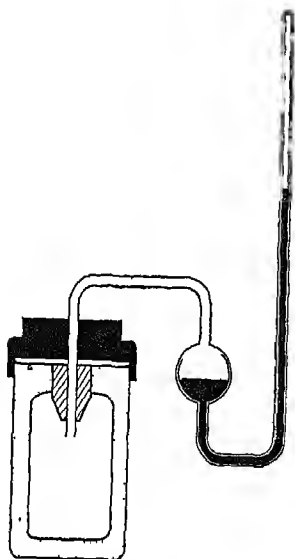


Figure 101 Diagram of Apparatus Used to Measure Osmotic Pressure

The diaphragm in this case is a porous cylinder in whose walls cupric ferrocyanide has been deposited.

34. Determination of Molecular Weights of Substances in Solution

As we have shown in the preceding sections, the lowering of the vapor pressure and freezing point, the elevation of the boiling point, and the osmotic pressure of a solution depend upon the relative number of molecules of solute mixed with a definite number of solvent molecules, and not upon the nature of the solute. This assumes, as we have previously emphasized, that the solute exists in

the solution in the molecular state, i.e., it is not an electrolyte, and it reacts in no way with the solvent. Two solutions containing the same number of molecules of two different solutes and the same number of molecules of the same solvent should therefore have the same osmotic pressure, boiling point, vapor pressure, and freezing point.

It has been found that one gram-molecular weight of sucrose, glucose, or glycerine, for example, dissolved in 1000 g of water, lowers the vapor pressure of water 0.31 mm, lowers the freezing point 1.86°C , elevates the boiling point 0.515°C , and exerts an osmotic pressure of approximately 22.4 atmospheres at 0°C . The osmotic pressure stated is the theoretical value. The observed value is usually a little higher than the one stated.

It is evident, therefore, that the molecular weight of any *non-electrolyte* can be determined from the properties of its solution as compared with those of a solution containing one gram-molecular weight of sucrose or any other non-electrolyte dissolved in 1000 g of the same solvent. The comparison is often made by considering freezing points. Let us say that 10 g of a substance, which we shall call x , when dissolved in 200 g of water, lowers the freezing point of the water 0.372° . *The molecular weight of the substance is that weight which when dissolved in 1000 g of water lowers the freezing point 1.86° .* Hence

- (1) 50 g of x lowers the freezing point of 1000 g of water 0.372°

$$(2) \frac{1.86}{0.372} \times 50 \text{ g.} = 250 \text{ g.} =$$

molecular weight of x .

The general equation is as follows.

$$\frac{\text{Grams of solute used}}{\text{g of water used}} \times \frac{1000 \text{ g}}{\text{g of water used}} \times \frac{1.86^{\circ}}{\text{observed lowering of freezing point}} = \frac{\text{molecular weight}}{\text{weight}}$$

This equation may also be used to determine the molecular weights of substances dissolved in solvents other than water if 1.86° is replaced by the lowering of the freezing point (Table 8) which is produced by one gram-molecular weight of any substance (subject to the same restrictions as before) in 1000 g of the selected solvent. This equation can also be used for calculations of the molecular weight from boiling point data by substituting the molar elevation of the boiling point (0.515° for water) in place of the molar freezing point depression constant (1.86° for water). The constants for different solvents are given in Table 8.

These methods of determining molecular weights are used for substances which cannot be studied as gases, either because they vaporize only at high temperatures, or because they decompose easily upon heating. The lowering of the vapor pressure and the osmotic pressure of the solution are seldom used as the basis of determining molecular weights because of difficulties in obtaining these measurements.

SOME FACTS AND THEORIES THAT HELP TO EXPLAIN SOLUBILITY

The solubilities of different substances, even in the same solvent, vary so greatly and depend upon so many factors that accurate predictions are not possible. Without ex-

TABLE 8

Lowering of Freezing Points and Elevation of Boiling Points of Different Solvents

Solvent	Boiling Point of Pure Liquid ($^{\circ}\text{C}$, 760 mm)	Boiling Point Elevation — 1 g-mol wt per 1000 g of solvent	Freezing Point of Pure Liquid ($^{\circ}\text{C}$)	Lowering of Freezing Point — 1 g-mol wt per 1000 g of solvent
Water	100°	0.515°	0.0°	1.86°
Benzene	80.2°	2.53°	5.5°	5.12°
Ether	34.6°	2.02°	-117.0°	1.79°
Carbon tetrachloride	76.8°	5.03°	-22.6°	2.98°

perimental evidence, one can never determine the quantity of one substance that will dissolve in a definite quantity of another, and frequently it is impossible to predict successfully whether or not a substance will dissolve in a given solvent at all. There are, however, a few qualitative rules or generalizations that are sometimes useful. Below we shall state some of these and also describe some of the theories that are helpful in understanding why certain kinds of substances are soluble in certain kinds of solvents but not in others.

35. The Solution of Ionic Compounds in Water

Because of the greater cohesion between their particles, ionic, or electrovalent, compounds dissolve less readily in many solvents than covalent compounds. The solid state of electrovalent substances consists of ions held in definitely fixed positions in crystal lattices by electrical forces. Hence, unless something happens to weaken these forces, the crystals do not dissolve in the solvent. Some solvents appear able to weaken the attraction of the ions for one another. The measure of this ability of the solvent is called its *dielectric constant*. The constant for water is relatively high, as compared with that of air as 1, water's dielectric constant is 78. This means that when water is placed between two oppositely charged metallic plates the charges on these plates attract much less strongly than when the space between the plates is filled with air or with another substance of lower dielectric constant than 78. We may think of water as exerting a similar influence upon the attraction of a positive for a negative ion in a substance such as sodium chloride. As a result of the decrease in the electrical attraction between the oppositely charged ions, the crystal structure of sodium chloride crumbles when placed in water. This means that a solution of sodium chloride in water is a mixture of particles (molecules) of water and ions of sodium and chloride. Just as there are no molecules in the crystalline state of sodium chloride,

neither are there any particles of this kind in its solution.

Using water as the most familiar solvent for substances such as sodium chloride, we may explain its action in producing a solution by reference to Figure 102. The water molecules may be thought of as electrical *dipoles* (page 153). The water dipoles tend to attach themselves to sodium and chloride ions in the crystal of sodium chloride in the manner indicated in Figure 102. The nega-

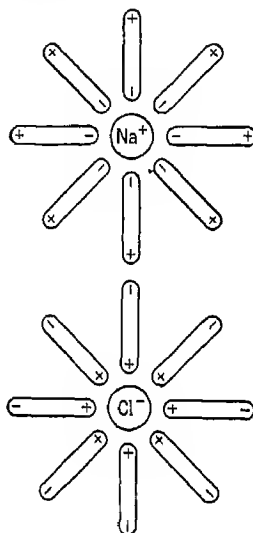


Figure 102 Water Dipoles Separating Sodium and Chloride Ions

tive ends of the molecules are attracted toward the positive sodium ion and the positive poles of other molecules are attracted toward chloride ions. Because of the orientation of water molecules around each ion, the attraction of each ion is satisfied, at least to some extent, and the ion of the opposite charge is less strongly attracted in solution than in the crystal.

The solubility of an ionic compound in a polar solvent must depend to some extent upon the relative ease with which the ions can be removed from the positions that they occupy in the crystal. The size of the ions, the quantities of charge that they carry, the number of electrons in their outside levels, and the manner in which the ions are ar-

ranged in the crystal result in differences in the rate of solution and in the quantities of different substances that dissolve in the same quantity of solvent

According to the theory that we have outlined above, ionic compounds should not be expected to dissolve in non-polar solvents, such as liquid methane or carbon tetrachloride (page 154). This, in general, is found to be true.

36 The Solubility of Gases

No doubt, the miscibility of gases in all proportions is possible because of the very weak attraction of their molecules for one another. If molecules of oxygen, for example, possessed considerable attraction for one another, they would tend to cling together in the presence of other gases, such as the nitrogen of the air, and mixtures could not be formed. Because this attraction is weak, the molecules of oxygen are practically independent and may freely and indefinitely diffuse among the molecules of other gases.

Gases, in general, are not very soluble in liquids. Those with relatively low boiling points, such as oxygen and hydrogen, are less soluble than those with relatively high boiling points. This behavior is in accordance with what we should expect, because when a gas dissolves in a liquid it must be converted into the liquid state. Naturally, those gases that are the most difficult to liquify, i.e., have the lowest boiling points, should prove less soluble, under comparable conditions, than gases that are easily converted to the liquid state.

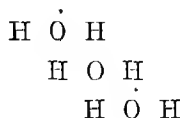
37. Factors that May Determine the Solubility of Solids and Liquids in Liquids

The melting point and the heat of fusion of a solid appear to be important factors in determining the solubility of the solid in a liquid. Since, when a solid dissolves in a liquid, it must be converted to the liquid state, solids that are easily liquefied, i.e., have low melting points and small heats of

fusion, should naturally dissolve more readily than those that melt only at very high temperature and that require relatively large amounts of heat to liquefy them.

In general, polar substances dissolve more readily in polar than in non-polar solvents. If both the solute and the solvent are composed of molecular dipoles, the molecules of the two substances will attract one another just as the dipole molecules of a single substance do. In such cases, this attraction must be one factor that leads to an intimate mixture of the molecules of the solute and solvent. Non-polar substances dissolve more readily in non-polar solvents than they do in polar substances. There is very little attraction between the molecules of a non-polar substance, and hence there is little resistance to the mixing of the more or less independent molecules of solute and solvent. Mixing results, in such cases, not from attraction between unlike molecules, but from the diffusion of the two kinds of molecules as a result of their kinetic energy. Thus, carbon tetrachloride dissolves very slightly in water, but it dissolves readily enough in benzene.

Hydrogen bonds (page 183) appear to play an important part in the formation of many solutions. In liquid water several simple H_2O groups are probably joined together to form larger molecular units (page 141). A hydrogen atom of one molecule probably shares an unused, or free, pair of electrons belonging to an oxygen atom of another molecule to produce the bonds that unite H_2O molecules.



A bond of this kind is, of course, a co-ordinate covalent bond. Since two molecules of water are bound together, in a certain sense by the hydrogen atom that is attached to the oxygen atoms of both of them, this bond is

sometimes referred to as a *hydrogen bond* or a *hydrogen bridge*

It is reasonable to expect that water molecules will form hydrogen bonds with others that contain $-OH$ groups in the same manner as they do with one another. Hence methyl alcohol, CH_3OH , dissolves in water, whereas benzene, C_6H_6 , and methane, CH_4 , do not dissolve in water, because, unlike oxygen, they do not contain atoms that possess unused electrons. Molecules of benzene and methane do not have strong attraction even for molecules of their own kind, hence they can easily form mixtures with molecules of other substances which, like themselves, have little or no attraction for one another. Water molecules, which associate with themselves, do not mix, however, with molecules of benzene, the fact that molecules of water tend to cling together prevents molecules of benzene from becoming dispersed among them.

Review Exercises

- How could you prove that a sample of a liquid is a solution and not the pure solvent?
- From the data given on page 195, calculate the weight of oxygen which will dissolve at 10 atmospheres of pressure in 100 ml of water ($0^\circ C$).
- What are the relative weights of oxygen and nitrogen which dissolve in 100 grams of water from the air at 0° and 760 mm?
- Describe the method commonly used to separate two miscible liquids.
- Describe the nature of the distillate and the changes in temperature which occur when a mixture containing nitric acid (75 per cent) and water is distilled.
- How are solubility curves, similar to those on page 198, constructed?
- How many grams of sodium nitrate will dissolve in 500 g of water at 30° ? Obtain data from the solubility curve.
- How many grams of solid potassium chloride will separate from a solution which contains 250 g of water and which is saturated at 70° if the solution is cooled to 30° ?
- From which substance, $NaNO_3$ or $NaCl$, could KNO_3 be more easily separated by fractional crystallization? Explain.

- What is meant by an *ideal solution*? What are some of the indications or lines of evidence by which the differences between a solution and the ideal condition for the same mixture of solute and solvent can be recognized?
- What is a solid solution? Give examples.
- Why does a solid which is composed of ions dissolve more readily in water than in solvents such as gasoline?
- What explanation can be offered for the limited solubility of gases such as oxygen and nitrogen in liquids? What explanation has been suggested for the tendency of chemically similar substances to dissolve in each other?
- Define solute, saturated solution, supersaturated solution, concentration, molar solution, normal solution, molal solution.
- Under what conditions are a molar and a molal solution almost identical (for the same solute and solvent)?
- How many grams of the following substances are contained in 1 liter of (a) 1/10 molar and (b) N/5 normal solutions? HCl , H_2SO_4 , $NaOH$, H_3PO_4 .
- Why does the solubility of any gas in water decrease with rise in temperature?
- How does a saturated solution differ from a concentrated solution?
- What volumes of the following liquids are required to give 1000 g of each?

Liquid	Specific Gravity
Benzene	0.878
Ethyl alcohol	0.785
Carbon tetrachloride	1.584
Ether	0.720
Carbon disulfide	1.293

- How many gram-molecular weights of each of the above solvents are present in 1000 grams? Compare the mole fractions of solvent in molal solutions of each of these liquids. Use the index to find the formulas of the liquids.
- State Raoult's law. Explain why a solution of a non-volatile solute has a lower vapor tension than the pure solvent.
- Apply Raoult's law to the boiling points and freezing points of solutions. Explain why solutions have higher boiling points and lower freezing points than the pure solvents.

23. A solution containing 20 g. of a substance in 150 ml. of benzene has a freezing point of 2.7°C . What is the molecular weight of the substance?
24. Define or explain: surface tension, viscosity, osmosis, osmotic pressure.
25. How could you determine whether a given solution is unsaturated, saturated, or supersaturated?
26. Can molar solutions of all salts, acids, and bases be prepared? Explain.
27. The formula for ethyl alcohol is $\text{C}_2\text{H}_5\text{OH}$. Knowing that it resembles sugar in its effects upon the properties of a solvent, calculate the volumes of alcohol and water which should be mixed to fill an automobile radiator which holds 15 liters, if the freezing point of the mixture is to be -15° . Assume that no change (this is slight) in volume occurs when the two liquids are mixed. The weight of 1 ml. of pure alcohol is 0.79 g.
28. How could you determine the molecular weight of a substance from the osmotic pressure of its aqueous solution?
29. What volume of 2 N sodium hydroxide solution is required to neutralize 200 ml. of 1 N sulfuric acid solution?
30. Ten milliliters of a solution containing 3.0 g. of sodium hydroxide per liter is required to neutralize 30 ml. of a solution of hydrochloric acid. What is the normality of the solution of the acid?
31. A solution containing 0.23 g. of glycerine in 10 ml. of water freezes at -0.465° . What is the approximate molecular weight of glycerine?
32. How would you proceed in the laboratory to produce the pure solvent from a solution containing (a) a gas, (b) another liquid, and (c) a solid?

References for Further Reading

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CLASSIFICATION OF THE ELEMENTS

*Where order in variety we see,
And where, though all things differ, all agree*

ALEXANDER POPE

THE PERIODIC TABLE

1. Introduction

The study of the elements has been greatly simplified by classifying them into a few families or groups, the members of which are very closely related in chemical, and often in physical, properties. Among the works of man there is no more beautiful example of our definition of science as classified and organized knowledge than this classification of the elements. We shall present, in this chapter, the classification based upon the work of Mendeleeff, who in 1869 laid the foundation of our scheme of classifying the elements by arranging them in the order of their *increasing atomic weights*. This is the arrangement, with a few changes, upon which our present Periodic Table of the elements is based. This table will be found on the inside back cover of this book.

2. Early Attempts at Classification

The general acceptance of the atomic theory was followed by many attempts to discover new elements and to classify those already known. The similarities of several elements were easily recognized and appeared to indicate natural divisions or families into which the elements then known could be classified. Thus, oxygen and sulfur were known to resemble each other in many respects, and it was soon evident that selenium and tellurium are also similar to them.

Calcium, barium, and strontium are closely allied metals. Chlorine, bromine, and iodine are non-metals which possess many properties in common. In accordance with these easily recognized relationships of certain elements, Dobereiner in 1829 suggested that elements possessing similar properties could be arranged in triads in which the atomic weight of the middle element was the approximate mean of the atomic weights of the first and third elements, and in which the properties of the middle element were about halfway between the corresponding properties of the first and third. Thus, bromine in the triad

Cl (35), Br (80), I (127)

is not as active an element as chlorine, but is more active than iodine. Under ordinary conditions, chlorine is a gas, and iodine is a solid. Bromine, between them, is a liquid. Even the atomic weight of bromine is approximately one half of the sum of the atomic weights of chlorine and iodine. Other triads suggested by Dobereiner were,

Ca (40); Sr (87), Ba (137)
P (31), As (75), Sb (120)

Attempts to classify the elements were centered mainly around the prospect of finding some property, common to all the elements, which could serve as a basis for the correlation of their similarities. Dobereiner

er's triads suggested atomic weight as such a property, since his triads consisted of elements in the order of their atomic weights. The first effort to classify all the elements in one system was made by Newlands in 1865. He suggested that the elements should be arranged in the order of increasing atomic weight. When this is done, as Newlands pointed out, the elements fall into well-defined series. The first series, beginning with hydrogen, contains elements which are very much like the elements that occupy corresponding positions in succeeding series.

Each of the series suggested by Newlands consisted of seven elements:

	1	2	3	4	5	6	7
Series (1)	H	Li	Be	B	C	N	O
Series (2)	F	Na	Mg	Al	Si	P	S
Series (3)	Cl	K	Ca	Cr	Ti	Mn	Fe

This classification suggests that certain elements are related in a manner somewhat similar to the notes in successive octaves in music. Thus, the first, eighth, and fifteenth elements should possess closely related properties. The second, ninth, and sixteenth should also be related to one another, as should also the third, tenth, and seventeenth elements. They should show, for example, similar tendencies to take part in chemical changes and should form closely related compounds.

Although there was some reason for confidence in the arrangement suggested by Newlands, it could not be accepted very generally as long as it threw elements as dissimilar as oxygen and iron in the same vertical group. Lesser, but still serious, inaccuracies are to be noted in the elements of the sixth and first groups. Manganese is not very closely related to nitrogen, and hydrogen in group one is, in many ways, entirely different from fluorine and chlorine. Attempts to extend the arrangement to the elements beyond iron (Fe) met with still less success. One serious difficulty in the way of any successful attempt at classification lay, of course, in the fact that the atomic weights of most of the elements had not yet

been determined accurately. Hence the exact order in which the elements should be placed could not be determined with precision. This lack of information often caused elements to be placed in vertical groups in which they clearly did not belong. Furthermore, many elements now known had not been discovered in Newlands's day. For many reasons, his ideas were not considered very seriously by other chemists. In fact, he was asked by one of his contemporaries if he had tried to classify the elements in the order of the initial letters of their names. Nevertheless, his efforts were a step in the right direction.

3 Mendeleeff's Periodic Classification

In 1869, Mendeleeff suggested a much more satisfactory classification of the elements than any previously published. In many respects Mendeleeff's scheme was similar to Newlands's octaves; indeed, the latter claimed for himself much of the recognition awarded to Mendeleeff for the periodic classification of the elements. Newlands does deserve credit for his early attempt to arrange the elements in the order of their atomic weights, the basis of classification also used by Mendeleeff. His classification, however, was far from complete and, as stated above, grouped together elements that possess almost no properties in common.

Mendeleeff's table, as we now know it (Figure 103), is divided horizontally into *periods* — rows across the table from left to right. Of these, hydrogen occupies the first by itself, each of the next two periods contains eight elements, which make a single row across the table and is called a *short period*. The others are *long periods*, each of these consists of two rows of elements. It will be noted, however, that all periods — short and long — begin with similar elements and end with similar elements, except of course the first period, which contains only hydrogen.

Prior to about 1898, the table consisted of eight (vertical) *groups* of elements. The eighth group contains three elements in each

Group \longrightarrow	0	1	2	3
Hydrides		RH	RH ₂	RH ₃
Oxides		R ₂ O	RO	R ₂ O ₃
Period 1		1 H 1 008		
2	2 He 4 003	3 Li 6 94	4 Be 9 02	5 B 10.82
3	10 Ne 20 183	11 Na 22 997	12 Mg 24 32	13 Al 26 97
4A	18 A 39 944	19 K 39 096	20 Ca 40 08	21 Sc 45.10
4B		29 Cu 63.57	30 Zn 65.38	31 Ga 69.72
5A	36 Kr 83 7	37 Rb 85 48	38 Sr 87 63	39 Y 88 92
5B		47 Ag 107 88	48 Cd 112 41	49 In 114 76
6A	54 Xe 131 3	55 Cs 132 91	56 Ba 137 36	57 La 138 92 *
6B		79 Au 197.2	80 Hg 200 61	81 Tl 204 39
	86 Rn 222	87 Fr 223 (?)	88 Ra 226.05	89 Ac 227.05 **

*Rare Earths Lanthanum Series (58-71)	58 Ce 140 13	59 Pr 140 92	60 Nd 144 27	61 Pm 147	62 Sm 150 43	63 Eu 152.0
**Rare Earths Actinium Series (90-96)	90 Th 232 12	91 Pa 231	92 U 238 07	93 Np 237	94 Pu 239	95 Am 241

4	5	6	7	8
RH_4	RH_3	RH_2	RH	
RO_2	R_2O_5	RO_3	R_2O_7	
6 C 12 01	7 N 14 008	8 O 16 00	9 F 19 00	
14 Si 28 06	15 P 30 98	16 S 32 06	17 Cl 35 457	
22 Ti 47 90	23 V 50 95	24 Cr 52 01	25 Mn 54 93	26 Fe 55.85
				27 Co 58 94
				28 Ni 58 69
32 Ge 72.60	33 As 74.91	34 Se 78 96	35 Br 79.016	
40 Zr 91 22	41 Nb 92 91	42 Mo 95 95	43 Tc 99 (?)	44 Ru 101 7
				45 Rh 102 91
				46 Pd 106 7
50 Sn 118 70	51 Sb 121 76	52 Te 127.61	53 I 126 92	
72 Hf 178.6	73 Ta 180 88	74 W 183 92	75 Re 186 31	76 Os 190 2
				77 Ir 193 1
				78 Pt 195 23
82 Pb 207 21	83 Bi 209 00	84 Po 210	85 At 211 (?)	

64 Gd 156 9	65 Tb 159 2	66 Dy 162 46	67 Ho 164 94	68 Er 167 2	69 Tm 169 4	70 Yb 173 04	71 Lu 171 99	
96 Cm 242								

Figure 103 The Periodic Table (Based upon Mendeleeff's Classification)
Atomic numbers above symbols of elements, atomic weights below

period, each group of three elements lies midway in a long series. The discovery of the inert gases of the atmosphere made necessary an additional vertical column, which came to be called the zero group. This group is sometimes placed just after group eight and sometimes just before group one. The position is of no importance, since the groups are continuous. We are to think of the table as arranged on a cylinder instead of a sheet. Hence, the zero group lies between groups eight and one, and its position on a flat table depends upon where we cut the cylinder when it is flattened out.

4. The Short Periods

Hydrogen is placed in the first period by itself in the table shown in Figure 103. Sometimes it is placed in group seven directly above fluorine, but more often it is placed above lithium and sodium in group one. Neither position for hydrogen is very satisfactory, because each locates the element in a group containing others that it resembles only remotely. Chemically, it is somewhat more like the metals of group one than like the non-metals of group seven.

Helium is the first element of the *second period* and stands at the top of the *zero group*. Beginning with lithium, which is a typical metal, there is a gradual change in the properties of the elements, as the atomic weight increases, until fluorine, a very active non-metal, is reached. The next element, neon, is unlike fluorine in almost every respect, fluorine is the most active of all elements, and neon is one of the least active. The existence of any compound of neon is doubtful. This element, however, resembles helium very closely — both are inert elements — and in keeping with the principle that the table should group together elements of similar properties, neon is made the second element in the zero group and is placed directly below helium in the table. This is the beginning of the *third period*.

Period 2	He	Li	Be	B	C	N	O	F
Period 3	Ne	Na	Mg	Al	Si	P	S	Cl
Period 4								
Row 1	Ar	K	Ca	Sc	Ti	V	Cr	Mn
Row 2		Cu	Zn	Ga	Ge	As	Se	Br

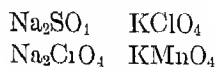
(Fe, Co, Ni)

When the seven elements next succeeding in the order of atomic weights are placed beneath the corresponding elements of the first horizontal row, it is found that very closely related elements are brought together in each of the columns. Thus, sodium is like lithium, magnesium like beryllium, aluminum like boron, silicon like carbon, phosphorus like nitrogen, sulfur like oxygen, and chlorine like fluorine. The similarities of the elements that form each of these pairs are readily seen when we consider the valence numbers of the elements and the formulas, and also the properties, of the compounds that they form.

LiOH	LiCl	BeO	BeCl ₂	B ₂ O ₃
NaOH	NaCl	MgO	MgCl ₂	Al ₂ O ₃
CO ₂	H ₂ CO ₃	CCl ₄	HNO ₃	NH ₃
SiO ₂	H ₂ SiO ₃	SiCl ₄	HPO ₃	PH ₃
H ₂ O	CuO	NaF	HF	
H ₂ S	CuS	NaCl	HCl	

5. The Long Periods

After chlorine, the next element is argon, the third inert element; it represents, therefore, the beginning of the *fourth period*. The next two elements resemble those of the first and second groups of the second and third periods. Thus, potassium resembles sodium, and calcium has many properties in common with magnesium. The next five elements, however, display many differences when compared with aluminum, silicon, phosphorus, sulfur, and chlorine, respectively. These differences are especially pronounced in chromium and manganese, which appear in most respects to belong to entirely different classes of elements than sulfur and chlorine. Whatever resemblances exist are illustrated in such compounds as



There are no compounds of chromium and

manganese with hydrogen or with metals that correspond to H_2S , HCl , Na_2S , or NaCl , and there are no compounds of sulfur and chlorine that correspond in properties to CrCl_3 , MnCl_2 , $\text{Cr}(\text{NO})_3$, etc. These differences indicate that chromium and manganese have properties more like those of metals, while chlorine and sulfur are in every sense non-metallic elements. The physical differences are also pronounced, chlorine is a gas, and sulfur is a yellow solid, chromium and manganese have the appearance and general physical properties of other metals. Because of these differences, the first elements of the fourth period are written under and a little to the left of the elements above them (Figure 103).

The next three elements (iron, cobalt, and nickel) certainly cannot be placed in the zero, first, and second groups, respectively, because their properties are entirely unlike those of argon, potassium, and calcium. They are placed, therefore, in an eighth group. It is not necessary that three groups be provided for these elements, because they are very closely related, placing them in the same group thus emphasizes certain family relationships. Because it resembles iron more than nickel does, cobalt is placed between iron and nickel, although strict adherence to the order of their atomic weights would place nickel second.¹

¹ A similar situation, in which the order of the elements as fixed by the order of the atomic weights fails, will be noticed in the positions occupied by potassium and argon. Although argon has the greater atomic weight, to place it after potassium would throw these two elements into groups where they clearly do not belong. These discrepancies, and also a similar one in the positions of iodine and tellurium, reflect somewhat upon the accuracy of the underlying principle of Mendeleeff's classification — the relation of the properties of the elements and their atomic weights. The discrepancies, which are here noted, indicate that something is wrong, that the atomic weights are not as sure a basis for classification as Mendeleeff believed. We shall learn in the next chapter that a classification based upon atomic numbers instead of atomic weights removes these difficulties and justifies the positions in the table that we have given to potassium, argon, iodine, cobalt and tellurium.

The elements following iron, cobalt, and nickel are placed in groups one to seven and a little to the right of the elements above them in the short periods. This arrangement places two elements in each group (one to seven) of the first long period, which consists of all the elements from argon to bromine. This period is called a long period, because two rows across the table are required between argon and the next element that resembles it — krypton. The first row of the long period is the *A* series, and the second row is the *B* series. Hence, in all the groups (one to seven) of this period, and of all the periods that follow it, the elements are divided into sub-groups designated by the letters *A* and *B*. The elements of the *B* sub-group resemble those of the short periods — second and third short periods — more closely than do those of the *A* sub-group, except in group one, where potassium, an *A* element, is much more like sodium than is copper, a *B* element. The elements in the first half of a long period from group three through group eight have many common properties including, in some types of compounds, the same valence numbers. These elements are sometimes called the *transition* elements of the period. In the third period the transition elements include those from scandium through nickel.

6 The Periodic Law

Because the arrangement of the elements in the order of their atomic weights causes them to fall into rows or "periods," Mendeleeff stated that *the properties of the elements are periodic functions of their atomic weights*. This statement is called the *Periodic Law*. It calls attention to the recurrence of properties in different elements when the elements are arranged in the order of increasing atomic weight. Thus, the properties of a very active metal occur in lithium, and the same general properties occur again in sodium, potassium, rubidium, and cesium. The chemical inertness of helium occurs again in neon, argon, krypton, and xenon. The periodicity

of properties, as revealed by the periodic classification, concerns physical as well as chemical properties. The elements display a definite periodicity, for example, in such properties as color, melting point, boiling point, hardness, conductivity of heat and electricity, magnetic susceptibility, specific gravity, compressibility, atomic volume, coefficient of expansion, malleability, ductility, and even places and forms of their occurrence in nature. Lothar Meyer first called attention to the periodicity of the physical properties of the elements.

7. Families of Elements

As we have seen, the horizontal rows of elements are called *periods*, and the long periods (argon to krypton, for example) are divided into *A* and *B* series. The vertical rows or columns of elements are called *groups*. These are numbered from 0 to 8, beginning on the left. Each of the groups (except the zero and eighth groups) is divided into two *families*, one containing *A* and the other *B* elements. Thus in group one there are two families of elements. (1) lithium, sodium, potassium, rubidium, and cesium; (2) copper, silver, and gold. The first of these families is called the alkali metals, and the second may be called the silver family. Here the elements of the short periods belong to the same family as the members of the *A* subgroup. In group seven, however, the elements of the short periods belong to the same family as the members of the *B* subgroup. This family consists of fluorine, chlorine, bromine, and iodine—the so-called *halogens*, or “salt-formers.”

Other important families are

- (1) The alkaline earths, Group Two, *A*.
- (2) The nitrogen family, Group Five, *B*.
- (3) The oxygen-sulfur family, Group Six, *B*.
- (4) The inert gases, Group 0. There are no *A* and *B* members of this group.

8. Another Form of the Periodic Table

A somewhat different arrangement of the elements to show their periodic classification

will be found on the inside of the back cover of this book. This periodic table is the same as that shown in Figure 103, page 220. The principal difference in the arrangement is that each of the long periods has been placed in a single row across the table. This arrangement places each family of elements in a different column. We have also placed the inert gases of the zero group on the right-hand side next to the non-metallic elements of group seven. This location seems to be somewhat more logical than the left-hand side of the table where they would be placed next to the most active of the metallic elements.

9. Predictions of Properties of Elements Based upon the Periodic Classification

Many of the properties of an element can be predicted from its period, group, and family. When Mendeleeff introduced his table, many positions were vacant. For example, in the third period the elements which we now know as scandium, gallium, and germanium were not known. Mendeleeff's arrangement required that elements fit into these three positions. For example, the next known element after calcium, in the order of atomic weights, was titanium, which could not be placed in group three, because it did not in any way resemble the elements of that group. It was apparent that the properties of titanium were very much like those of the elements of group four, but if it were placed in that group, a blank was left in group three. Furthermore, the difference between the atomic weights of calcium and titanium was seen to be 78, a difference considerably greater than that between other consecutive elements in the table. Likewise, there appeared to be a difference of about 10 in the atomic weights of zinc and arsenic.

The facts enumerated above were the basis of Mendeleeff's prediction that three gaps existed in this portion of the table, and that these would be filled some day by new elements. Mendeleeff named the three hypothetical elements *eka-boron*, *eka-aluminum*,

and *eka-silicon*, the prefix *eka* meaning *after* or *following*. He even went so far as to predict the properties of these elements. Within a few years after his predictions, the three elements were discovered, largely because chemists were encouraged to seek them and to test the accuracy of the periodic classification by proving or disproving the predictions that Mendeleeff had based upon it. The properties predicted for *eka-silicon* and those actually belonging to germanium, as this element came to be called, are given below for comparison.

Predicted Properties of Eka-Silicon	Properties of Germanium (1886)
Atomic weight 72	72.3
Specific gravity 5.5	5.47
Color, gray	grayish-white
Valence, 4 toward oxygen	4
Oxide, a white solid, XO_2	white solid, GeO_2
sp. gr. 4.7	sp. gr. 4.702
Chloride, $XC l_4$, volatile liquid	volatile liquid
b. p. below 100°	b. p. 86°
sp. gr. 1.9	sp. gr. 1.9
Acted upon by acids only slightly	Does not react with HCl
Does not react readily with solutions of bases	Does not react with solutions of KOH

Several other properties, which we need not enumerate here, showed an equally satisfactory agreement between prediction and observation. The properties of scandium and gallium were predicted with similar precision. Mendeleeff's table thus survived the tests of prediction and discovery, and in doing so, gained favorable and general recognition.

Late in the nineteenth century, the discovery of the inert gases served as another and a more severe test of the system. These elements constitute a complete group which must be accommodated as a unit somewhere in the table. The original table proposed by Mendeleeff had no place for this new family of elements. All the groups from one to seven, as well as the transitional eighth group were fairly complete and the properties of their elements were well established, this was particularly true of the valences of these elements. Since the inert elements do not combine with others and therefore always possess zero valence, it was evident that they should be placed in a "zero group" located to the left of group one. When this was done, each member of

this group was found to fit exactly into the proper position with respect to its atomic weight. Thus helium's atomic weight is just below that of lithium, neon falls between fluorine (19) and sodium (23), krypton (82.9) between bromine (79.9) and rubidium (85.4), and xenon (130.2) between iodine (126.9) and cesium (132.8). Radon falls between numbers 85 and 87, whose atomic weights remain undetermined. The only failure of an inert element to fall in its proper position occurs when we consider the position of argon. The atomic weight of this element is 39.9, while that of potassium is 39.1, hence, strict adherence to the order of increasing atomic weight would place argon after potassium, or in group one. This discrepancy, however, is no more serious than others which occur in well-established groups, and does not weaken materially the arrangement suggested. It does make us question, however, the use of atomic weights as the basis of determining the order of the elements in the periodic table.

10. Valence Numbers of Elements in the Different Groups of the Periodic System

The most striking similarity of the elements within a group is seen in their valence numbers. Indeed, this is sometimes the only likeness. The maximum valence of the elements in their oxides increases one unit at a time from group one to group seven. If we express combining capacities in terms of the valence of the hydrogen atom as unity, the sodium atom in group one combines with as much oxygen as the hydrogen atom (Na_2O and H_2O), and its valence number is therefore 1. This is true of the other elements of this group. Thus we have K_2O , Ag_2O , Cu_2O , etc. One atom of an element in the second group combines with as much oxygen as two atoms of hydrogen, and thus we have the oxides of these elements MgO , CaO , HgO , CdO , ZnO , etc. In group three we have B_2O_3 , Al_2O_3 , etc.; in group four, CO_2 , SiO_2 , PbO_2 , in which the elements combine with as much oxygen as four atoms of hydrogen; in group five, N_2O_5 , P_4O_{10} , As_4O_{10} , and others represent the maximum valence number of these elements toward oxygen. In group six, SO_3 and CrO_3 are representative

Group								
0	1	2	3	4	5	6	7	8
								+ 8
						+ 6	+ 7	
					+ 5		+ 5	
				+ 4		+ 4		+ 4
			+ 3		+ 3		+ 3	+ 3
	+ 1	+ 2		+ 2			+ 1	+ 2
Free Element, Valence Number, 0								
								- 1
				- 4	- 3	- 2		

Figure 104 Valence Numbers and the Periodic Table

The valence numbers are those that are most prominent for the elements of each group. Not all the valence numbers for all the elements of any group are shown.

oxides, and in group seven oxides such as Cl_2O_7 , or compounds corresponding to them, indicate that these elements can have a maximum valence number of 7. Among the elements of group eight at least one element, osmium, forms an oxide (OsO_4) in which the valence number is 8. Usually, however, the valence number of the transitional elements is 2, 3, or 4, as in FeO , Fe_2O_3 , etc. As we begin a new horizontal row (period) in the table, the valence number drops to zero, increasing again one unit at a time in succeeding groups.

So far we have considered the valence numbers of the different elements in oxides, in which we may compare their combining capacities with that of hydrogen. Many of these elements also combine *with* hydrogen. In this respect the valence numbers of the elements in the different groups vary from zero, for the inert gases, to 4 for the elements of group four. Thus the formulas of typical hydrogen compounds are NaH , CaH_2 , and CH_4 . In like manner, the valences with chlorine also increase from zero to 4 as illustrated by NaCl , MgCl_2 , BCl_3 and AlCl_3 , CCl_4 , etc. Beginning with group five, how-

ever, the valence with hydrogen decreases one unit per group. Thus, in group five, NH_3 , and PH_3 are typical hydrides, in group six, H_2O , H_2S , H_2Se , etc., and in group seven, HCl , HBr , and HI are representative.

11 Changes of Properties Within Groups

The valence numbers of the elements of the eighth group vary widely, although osmium and ruthenium sometimes have a valence of 8, as we might expect. The similarities of these elements are very marked within a given period, but considered as a (vertical) group, the elements differ greatly. Thus, iron, cobalt, and nickel are very closely related, but there is very little likeness between them and osmium, rhenium, and platinum.

Within a (vertical) group of elements there is a gradual change of properties from top to bottom. These changes are by no means as profound or as sharp as are the changes within a period — from left to right. In a period the elements change from very active metals on the left to typical non-metallic elements on the right. There is also the well-ordered increase in valence (toward oxygen) from one group to the next. Within a group, the valence of all the elements is identical, or at least they have *one* valence number in common. There is, however, a slight change in the metallic character of the elements within a group. This change indicates a tendency of metallic properties to become more pronounced with the increasing atomic weights of the elements. Thus, cesium (if we neglect number 87 about which we know very little at the present time) is the most active metal in group one. In fact it is the most active metal in the entire system of elements. Similarly, bismuth in group five (B) is much more metallic in character than the other elements of this family. This difference is especially pronounced if we compare bismuth with nitrogen, the first and lightest member of the family. Iodine, in group seven, although a typical non-metal, is the least active of the halogens and in many respects differs much less from the metals than fluorine, chlorine, and bromine. Fluorine and chlorine are gases under ordinary conditions, bromine is a volatile liquid, and iodine is a solid. Thus, even in a physical sense, iodine is more like the metals than the other elements of its family.

Just as metallic properties within a group increase with increasing atomic weight, conversely it may be said that the elements at the bottom of the different groups are less non-metallic in character than those at the top. Thus, boron, carbon, nitrogen, oxygen, and fluorine are all much more non-metallic in chemical behavior and in their physical properties than are thallium, lead, bismuth, tellurium, and iodine. Fluorine, at the top of group seven, is the most active of all the non-metals. It combines with so many elements and reacts with so many substances that it is extremely difficult to find a container for it when it is produced. Because of its extreme activity in combining with other elements, it tends to remain in the combined state. Hence its production in the free state is also very difficult.

If we draw a line across the periodic table (Figure 103) in a diagonal direction from the upper left-hand corner to the lower right-hand corner, the table is divided roughly into two divisions of elements. Those on the left are the metals, those on the right are non-metals. As might be expected, the elements which lie along or near the diagonal line exhibit the properties of both metals and non-metals. Thus, arsenic and antimony resemble the metals in compounds such as AsCl_3 and SbCl_3 , which are somewhat like the chlorides of sodium and calcium (NaCl and CaCl_2). These elements also form compounds such as H_3As and H_3Sb , which are like the hydrides of nitrogen, sulfur, and chlorine (NH_3 , H_2S , and HCl). They also form compounds, such as H_3AsO_4 and H_3SbO_4 , in which they resemble sulfur in the sulfates (H_2SO_4).

12. Uses of the Periodic Table

The periodic table brings together in the same group elements that possess similar properties. It also displays the gradual changes in properties that occur from group to group within a period (across) and from top to bottom within a group. Such a classification is of inestimable value to the student. It allows the different elements to be studied as a few well-defined groups, or families, rather than as ninety individual substances. For example, an acquaintance with the periodic table allows one to predict, as Mendeleeff predicted for eka-silicon, many

of the properties of an element, although one may not previously have studied that element. As an example, we should expect that cesium, since it is in group one and is an A element, would form a chloride having a formula (CsCl) and properties similar to those of sodium chloride, NaCl . Through this system of classification, therefore, our knowledge of all the elements and their compounds is correlated, and the chemistry of each element becomes a part of a well-organized outline including all of them.

Secondly, the system as suggested by Mendeleeff led to more accurate determinations of the atomic weights of the elements than had previously been available. The atomic weights of some of the elements were not accurately known in 1870. Indium, for example, was thought to be bivalent, and because its equivalent weight was known to be about 38, its atomic weight was thought to lie between 75 and 76. The periodic table indicated that this value was not correct, because it would place indium between arsenic (75) and selenium (79.2), where it obviously did not belong. However, there was a gap in the table, as it then stood, between cadmium (112.4) and tin (118.7), and it was seen that the general properties of indium would fit into this group-three position much better than into group six. If indium were placed here, it should have a valence of 3, its oxide should be In_2O_3 , instead of InO , and its atomic weight should be 3×38 , or about 114, instead of 2×38 , or 76. Later investigations of the properties and atomic weight of indium proved that these assumptions were correct. Accordingly, this element was placed in its logical position in the table. Similar corrections were made in the atomic weights of other elements.

The table has also been of great value in checking the properties of the elements, if the data obtained by experiment did not agree with the data that could be predicted from the location of the element in the table, the facts had to be carefully checked.

Lastly, the periodic classification has en-

couraged the search for new elements, because blanks in the table as it was first constructed indicated that certain other elements existed. We have already described Mendeleeff's prediction of the three elements that belong below boron, aluminum, and silicon in the table, these and other gaps have been filled. The search has slowly narrowed until at the present time it can be stated without serious question that none of the ninety-two positions from hydrogen to uranium remain unfilled. More important still is the fact that a place in the table has been found for every element that has been discovered. Although it appeared, at first, to be a purely arbitrary scheme that by chance did bring together elements of similar properties in the same group, the periodic classification has been completely justified by the results that it has yielded.

13. Weaknesses of Mendeleeff's Periodic System

Our commendation of the periodic system must not pass, however, without mention of certain weaknesses in it, many of which we have already discussed in connection with various features of the table (page 223). These and others are summarized below.

(1) The position of hydrogen is uncertain (page 222).

(2) Some elements must be shifted from the positions to which they would be assigned by strict adherence to the order of increasing atomic weights. This shift is necessary in order to bring such elements into groups with other elements which they resemble and to avoid placing them in groups whose members they do not resemble in chemical behavior or, in some instances, even in physical characteristics (page 223).

(3) Mendeleeff's classification places some elements in groups to which they properly belong only if a minor valence, and perhaps other somewhat unusual properties, of the element are considered. Thus, copper in group one does have a valence of one toward oxygen, one of its oxides has the formula Cu_2O , and the corresponding chloride is CuCl . But the more common and important compounds of copper are those in

which this element has a valence of two — CuO , CuCl_2 , etc. Many of the elements have more than one valence toward oxygen. Thus, there are two oxides of carbon, five of nitrogen, two of mercury, two of sulfur, etc. The position of each of these elements in the periodic system, of course, emphasizes but one of these valences and but one set of corresponding compounds.

Some families contain members that resemble elements in other groups more than those of their own group. Mercury of group two and copper are probably more closely related than are copper and gold, both of which are in group one.

(4) A large group of very closely related elements — the rare earths — must be placed in the table between cerium and hafnium. To accommodate these, the form of the lower part of the table must be altered considerably. They are usually omitted from the table proper and placed in a group by themselves at the bottom.

(5) There is no relation between the periodic classification and other methods of classifying the elements. The metallic elements of the activity, or electrochemical series, follow no order which can be traced in the periodic table; they are scattered here and there throughout this table. Furthermore, the schemes of analysis of substances containing different metals call for the separation of these elements into certain well-defined groups. In some of these groups the metals are, for the most part, those that belong to the same group in the periodic classification. This is true particularly of the analytical group that includes sodium and potassium and the group containing calcium, barium, and strontium. In others, the metals are scattered throughout the table. One such group, for example, contains such widely separated metals as copper, cadmium, bismuth, and mercury, another contains lead and silver, and still another brings together for detection iron, aluminum, manganese, zinc, and chromium.

Mendeleeff's classification of the elements was based upon the simple principle of arranging the elements in the order of increasing atomic weights. This principle, however, does not explain the table — it does not show why the elements, when so arranged, fall into periods and groups. Mendeleeff himself had no explanation of the table and was of the opinion that there was no suitable ex-

planation so far as was known at that time. No one knew any way of explaining, for example, the fact that atoms of sodium have many properties similar to those of potassium but few, if any, similar to those of chlorine. Also, there was no clue that even suggested an explanation of the gradual changes from group to group within a period or from top to bottom within a family. It was evident, certainly, that atomic weights alone could not explain all the similarities and differences, because sometimes the order of atomic weights had to be abandoned in order to place some of the elements in the group to which they belonged.

Many of the apparent defects of the periodic classification have been explained, and others have been corrected, as we shall show in the next chapter, by using atomic numbers instead of atomic weights as the basis of classification. With all its defects the periodic table has served so well and has proved so accurate in many ways that such weaknesses as have been described scarcely can detract from the profound respect with which one must regard it. No other principle or theory has done so much in producing a systematic classification of chemical knowledge.

Review Exercises

1. Explain the following terms as they are used in describing parts of the periodic table: period, A and B series, group, family.
2. State the Periodic Law. Show that it is not entirely valid as Mendeleeff formulated it.
3. How do the properties of the elements change (a) from left to right and (b) from top to bottom in the table (1) with regard to valences toward oxygen, (2) with regard to valences toward hydrogen, and (3) with regard to metallic characteristics?
4. What are some of the weaknesses of Mendeleeff's classification?
5. What does the periodic system suggest concerning the nature of atoms?

6. How has the periodic classification aided in the development of chemistry?
7. From their positions in the periodic table, predict the formulas of oxides of the following elements: Mo, W, Si, Sn, Sb, Te, and Ra.
8. Would you expect the chloride of silicon to resemble NaCl more closely than it does CCl_4 ? Explain.
9. Which element, iodine or chlorine, should combine more readily with sodium? Explain.
10. Which element, nitrogen or bismuth, should combine more readily with chlorine? Explain.
11. From its position in the periodic table, predict the properties of sulfur as compared to those of oxygen.
12. Of the three elements calcium, strontium, and barium, which should occupy the highest position in the activity or electrochemical series? Explain.
13. What atomic weights would you predict for elements 85 and 87?
14. Would you expect tellurium and selenium to resemble sulfur more closely than they resemble chromium? Explain.
15. Of the three elements, sulfur, mercury, and tin, which would you predict is most likely to form a hydroxide that can act as an acid? Explain.

References for Further Reading

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X-RAY SPECTRA, ATOMIC NUMBERS AND THE STRUCTURES OF CRYSTALS

Nature reveals the same wide grandeur in the atom and the nebula, and each new aid to knowledge shows her vaster and more diverse, more fruitful and more unexpected, and, above all, unfathomably immense

PERRIN

1 Introduction

Atomic numbers and the methods used to determine them are discussed in this chapter in order that we may complete the study of the periodic classification of the elements that we began in the preceding chapter. We shall find that a classification based upon the atomic numbers of the elements is more satisfactory in some respects than Mendeleeff's classification, which was based upon atomic weights.

We shall also discuss in this chapter the structures of crystals, because the methods used to study crystals and to determine atomic numbers are very similar. Both involve the effects of crystals upon X-rays

called *cathode rays* (page 258). The particles of which they are composed are electrons. In 1895, Roentgen discovered that these "rays" have a peculiar effect upon the glass walls of the tube and upon other articles which they strike. Thus, in Figure 105, the rays are made to strike a target, which is made of some metal. Whenever the cathode rays strike, a disturbance is produced and is transmitted, as radiant energy, from the point of origin through space with the same velocity as visible light. These rays differ from visible light in many respects, however. For one thing, they are much more penetrating. Technically speaking, they are made up of shorter wave-lengths than rays

2 X-Rays

An electric current will pass through a gas contained in a tube in which the pressure is very low. A tube of this kind is shown in Figure 105, in which *A* and *C* are the anode and cathode, respectively. As the discharge occurs, the gas within the tube emits light, and certain "rays" appear to stream off the cathode. These are not true rays like light; experimental evidence indicates that they consist of very small, negatively charged particles, which travel in straight lines with enormous velocities. They are

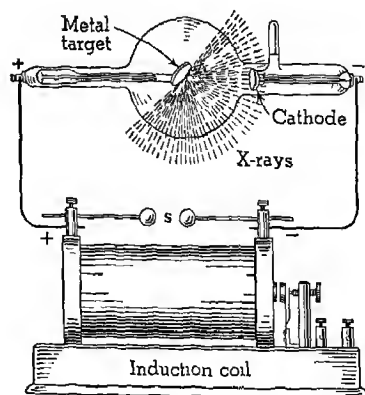


Figure 105 X-Ray Tube

of visible light. They are invisible to the eye, but like visible light they affect the photographic plate and in a far more effective manner than visible light. They are commonly called *Röntgen rays* or *X-rays*.

Because of their greater penetrating power, X-rays pass through substances that are opaque to visible light. Thus, a photographic plate wrapped in several thicknesses of black paper is unaffected by exposure to visible light but is affected by X-rays in a pronounced manner. The use of X-rays in revealing fractured bones of the body, and in other diagnostic treatments, depends upon the relative ability of different parts of the body, such as bones and flesh, to absorb, or stop, the rays. The rays are also stopped by thin sheets of metals, such as lead.

Light and other forms of radiant energy can be considered as wave motions, like the waves which are produced by the dropping of a stone into water. In the case of water waves, a whole series of crests and troughs are produced and the wave travels out in ever-widening circles. We may think of light and X-rays as similar waves which travel out through space from some point of disturbance in an expanding spherical shell. These waves may be considered as also having crests and troughs. The distance between two successive crests is a *wave-length* (Figure 106). Light and other forms of radiant energy also are said to differ in frequencies, the smaller the wave-length, the greater the frequency. This means that there will be more wave-lengths per centimeter, in the direction in which the wave is

moving, for small wave-lengths than for larger ones.

SPECTRA OF VISIBLE LIGHT AND X-RAYS

In studying many of the elements and their compounds the chemist makes frequent use of data obtained by determining the wave-lengths or frequencies of the light emitted by different substances when they are made luminous, i.e., when they are heated to a temperature at which they emit light. In later chapters, we shall have occasion to refer to this subject again. Just now, we are interested in the wave-lengths and frequencies of the X-rays emitted under suitable conditions by different elements and their compounds. To understand the methods used in determining the wave-lengths of X-rays we shall find that a brief description of the methods used in the study of visible light will be helpful.

3 The Spectroscope

Sometimes the chemist finds that he cannot use ordinary chemical methods to identify certain elements or their compounds. For example, the inert gases of the atmosphere, which form few if any compounds, cannot be identified by their chemical reactions. Instead, the chemist in studying them must use a device borrowed from the physicist and called the *spectroscope*. This is an instrument which breaks up a beam of light from any source into its various colors, or wave-lengths. A common form of spectroscope contains a glass prism which resolves a beam of light into its different components. Another form employs a diffraction grating which consists of a number of lines ruled closely together on a glass plate. We shall briefly describe the action of the former.

Ordinary, or white, light is made up of all different colors—red, orange, yellow, green, blue, and violet. Each of these colors

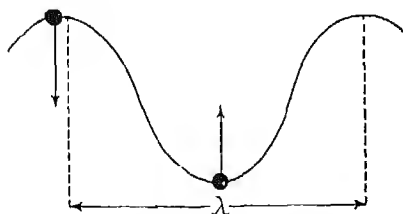


Figure 106 A Wave of Light or X-Rays is Thought to be Somewhat Like a Water-Wave

The distance from one crest to the next is a wave-length

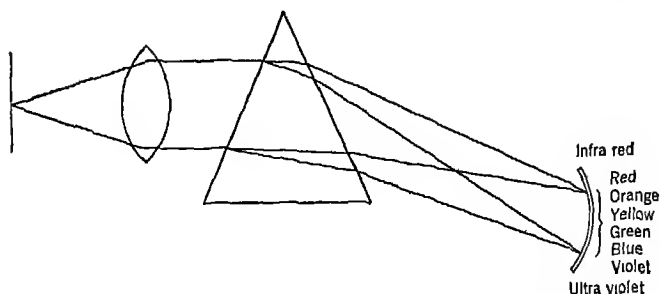


Figure 107. Production of a Spectrum by Means of a Prism

consists of light waves of several different lengths (Figure 106). When the beam is passed through a prism (Figure 107), each kind of wave is bent or *refracted* in a definite manner, and the different waves are refracted to different extents. Red light is refracted least, violet most, and the other colors to an intermediate extent. In the spectroscope, the beam of light enters A (Figure 108) through a narrow slit, which is located so that it is parallel to the axis of the prism. After refraction, the different colors of light give numerous images of this slit, when they fall upon a screen which is placed in the proper position with reference to their path after deflection. Or, if we substitute an eyepiece (B) for the screen, the different images of the slit appear to the eye as bright lines on a dark field. We speak, therefore, of the *lines of the spectrum*. For white light the series of lines is complete — all colors are represented — and the spectrum is said to be continuous. The spectroscope usually

has another tube (C) containing a scale that is observed when one looks through the eyepiece. The different lines of the spectrum are scattered out along this scale. If the same scale is used, and if it is fixed in position, any one line can be identified in any spectrum by its location on the scale.

4. Spectra of Light Emitted by Luminous Materials

White light may be produced by heating any solid to incandescence, consequently, light from such sources gives *continuous spectra*. *Discontinuous spectra* are obtained from the light emitted when salts of the metals are volatilized in a flame, or when gases of different kinds are subjected to an electrical discharge under low pressures. The light from such sources is resolved into spectra that contain only certain bright lines. These lines are characteristic of the elements contained in the salts which are volatilized or are present in the gases subjected to the

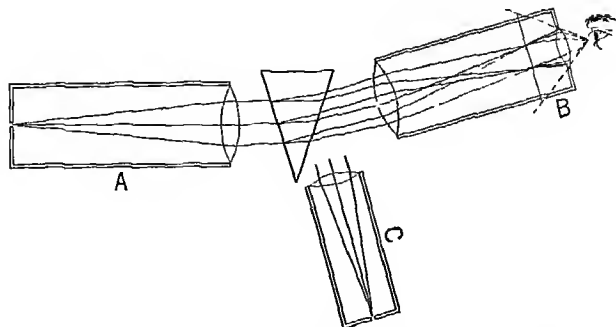


Figure 108. The Essential Parts of a Spectroscope

electrical discharge. It is possible, therefore, to identify an element by means of the spectrum of the light which it emits.

The common method of causing the metals to emit light, so that their spectra may be produced, consists in heating small quantities of their salts (usually the chlorides because they as a rule are most volatile) on a platinum wire in the flame of a Bunsen burner. The burner is placed before the spectroscope in a position so that the light from the flame will pass through the slit. The beam of light selected by the slit falls upon the prism, there it is analyzed and the spectrum is observed through the eyepiece. To secure the higher temperatures sometimes required to volatilize certain substances, the electric arc may be used. The carbon electrodes of the arc may be hollowed out on the end to make small cups in which the substance to be volatilized is placed. The arc flame may reach a temperature of about 3000°C . The light from this source gives an *arc* spectrum. The terminals of an induction (spark) coil may also be coated with the substance to be volatilized. The light from this source gives a *spark* spectrum. Flame, arc, and spark spectra differ in the number of lines which can be observed in each. A substance that shows some of the characteristic lines of the spectra of its constituent elements when heated in a flame will reveal more lines when its spectrum is determined by the arc and spark methods.

Gases are usually made luminous by discharging electricity through them under a pressure of about 1 mm. The tubes are sealed after the re-

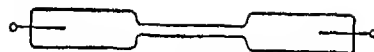


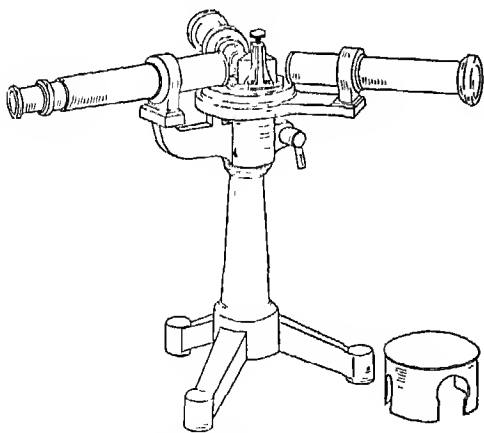
Figure 110. A Plücker Tube

moval of air and the introduction of very small quantities of the gases to be studied. Two electrodes (platinum wires) are sealed through the walls, one wire at either end of the tube. The central portion of the tube is usually constricted until it is of capillary dimensions (Figure 110). This is the so-called Plücker vacuum tube.

The tube is placed before the spectroscope, and the light emitted by the gas in the capillary portion of the tube is passed through the slit. The lines of the spectrum obtained from this source depend largely upon the nature of the gas in the tube. The color of the light in the tube and the character of the outstanding lines in the spectrum differ, however, for the same gas with the pressure in the tube and with variations in the nature of the electrical discharge, e.g., whether it is intermittent, continuous, oscillating, etc.

5 Absorption Spectra

If a substance which is either in the gaseous state or in a solution (light must pass through it) is placed between the slit of the spectroscope and some source of white light, an *absorption* spectrum can be obtained. Instead of a continuous spectrum, certain lines, depending upon the nature of the absorbing medium, fail to appear and are represented by black lines (absence of color). These are called *absorption lines*. The positions of the black lines in the absorption spectrum of a substance correspond exactly to the bright lines of the spectrum which the same substance produces when it is made to emit light. Thus, certain black lines appear when the light from the sun is analyzed. These are called *Fraunhofer* lines and are the result of the absorption of certain waves by the gaseous substances contained in the sun's atmosphere. By studying these absorption lines it has been possible to identify the elements producing them, and hence the character of the atmosphere surrounding the sun. Helium, for example, was recognized as an element in the sun long before it was discovered on the earth. Certain absorption



Courtesy of Arthur H. Thomas Company

Figure 109. A Spectroscope

lines were observed in the spectrum of the light from the sun. These lines could not be identified in the spectra of any of the elements known on the earth, and were said, therefore, to be produced by an element which existed only in the sun or its atmosphere. Later, the element was discovered on the earth and was identified by the lines in its emission spectrum, which corresponded exactly with the absorption lines previously observed in the sun's light.

6 The Complete Spectrum

Visible light, as shown in Figure 111, includes only a small fraction of all the known wave-lengths of radiant energy. The complete spectrum includes longer wave-lengths, such as those of infrared radiation, and the shorter wave-lengths of ultraviolet light and X-rays. The ordinary spectroscope can be used to resolve a beam of visible light into its different wave-lengths, but it cannot be used for other parts of the spectrum. We shall now turn our attention to the method used to produce X-ray spectra.

7. X-Ray Spectra of the Elements

In 1914, Moseley found an important relationship between the atomic number of an element and the wave-lengths of the X-rays emitted by the element when it is bombarded by cathode-ray particles (electrons) in an evacuated tube. To analyze the X-rays emitted by an element, i.e., to determine the spectrum of these X-rays, Moseley selected a narrow band of X-rays by means of a slit in a box made of sheets of lead and enclosing

the tube. This small band or pencil of rays was allowed to fall upon a face of a crystal, which acted in the same manner upon the beam of X-rays as a diffraction grating does upon light. A grating consists of very closely ruled parallel lines upon a glass plate. Such a grating breaks up a beam of light into its constituent colors, or wave-lengths, thus producing a spectrum. In order to produce a spectrum the lines of the grating must be properly spaced, this requires that the distances between successive lines must bear the correct relation to the wave-length of the light which passes through the openings, or slits, between the lines of the grating. In general, the distance between successive slits must be of the same order of magnitude as the length of the light waves. When this condition is fulfilled, a series of dark and light lines appear on a screen placed on the opposite side of the grating from the source of light. The dark lines, denoting the absence of light of any kind, are caused by the interference of the waves which spread out in spherical shells from the slits between the lines. The bright lines are produced when reinforcement of one wave by another occurs. By interference we mean that waves from different slits meet trough to crest, such waves extinguish each other. By reinforcement we mean that the crests of different waves coincide. The exact positions at which the reinforced waves will strike a screen on the opposite side of the grating from the source of the light depends upon the wave-length of the light. Different wave-lengths will show reinforcement at different positions with the same grating. This means

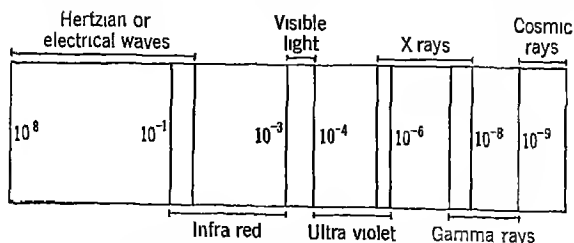


Figure 111 The Complete Spectrum
Numbers refer to wave-lengths (in mm)

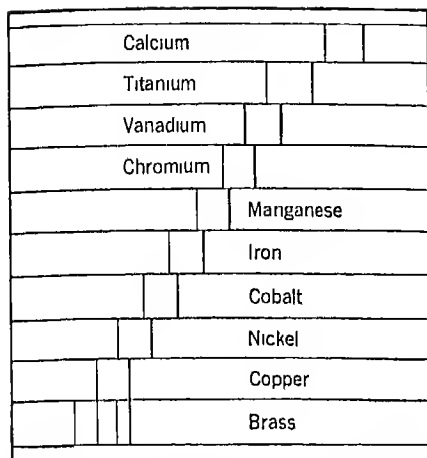


Figure 112 X-Ray Spectra Showing the Decrease in Wave-Length (toward the left) as the Atomic Numbers of the Elements Increase

that the rays of red light will appear at one position on the screen and blue at another. In this way a spectrum of light is obtained.

The wave-lengths of X-rays are so small in comparison to those of visible light that lines cannot be ruled sufficiently close together on a grating to produce an X-ray spectrum. The situation is much like the attempt to produce a spectrum of ordinary light by passing it through a grating consisting of lines a foot apart, or, let us say,

trying to produce the same effect by means of a picket fence.

In 1912, Laue found that a crystal can be used to diffract, or break up, a beam of X-rays into individual wave-lengths in the same manner that a ruled grating diffracts visible light. This showed that the particles of a crystal are arranged in definite planes and lines, and that these are very close to one another. The rows of atoms, or other particles, in a crystal act in a manner similar to the ruled lines of the diffraction grating. The beam of X-rays is thus resolved by the crystal into its different wave-lengths, and we say that an X-ray spectrum is produced.

8 Determination of Atomic Numbers of Elements from Their X-Ray Spectra

Moseley analyzed the X-rays which result when different elements are subjected to bombardment by cathode-ray particles and thus are made to serve as the source of rays. He found that the spectra of the elements show certain characteristic differences. The same lines, or pairs of lines, appeared in the spectrum of the rays produced by successive elements, as these were studied in the order of their atomic numbers. The wave-lengths, or frequencies of these characteristic lines,

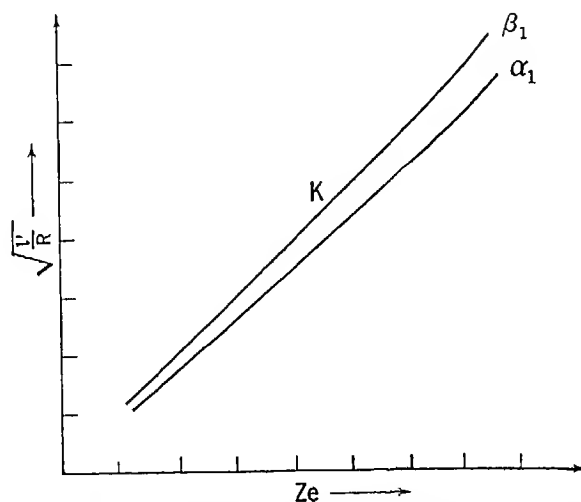


Figure 113 The Relation Between the Frequency of X-Ray Spectral Lines and the Atomic Numbers (Ze) of the Elements that Produce the X-Rays

The frequencies used here are those of the α_1 and β_1 lines of a series (K) in the X-ray spectrum.

however, were found to vary in a regular fashion from one element to the next (Figure 112). When Moseley plotted against the atomic weight the frequency or wave-length of a particular line that appeared in the X-ray spectra of many elements, he found only an approximate relationship. The points when connected gave an irregular line. It tended always in the same direction, but it was not straight. He then plotted the square roots of the frequencies against the atomic numbers of the elements. This gave an almost straight line (Figure 113), which showed that the X-rays emitted by an element depend upon the atomic number of the element rather than upon the atomic weight. If the wave-length, or frequency, of this same line can be determined for an element, then the atomic number of that element can be determined directly from the curve. This method has often been used in the identification of some of the elements.

9. Atomic Numbers and the Periodic System

The classification of the elements in the order of their atomic numbers, as determined by Moseley's method, has certain advantages over the classification based upon atomic weights. In the first place, the elements, when so classified, fall into position in the groups to which they belong. No exceptions, such as were made in the positions of argon and potassium in Mendelceff's table, have to be made. In the second place, the number of elements between hydrogen and uranium is definitely fixed. There can be only 90 elements within these limits. Blanks in the system were rapidly filled after Moseley's method of identifying an element by its X-ray spectrum was developed. Within a few years after Moseley's untimely death in 1914, hafnium, masurium, rhenium, and thulium were discovered by means of their X-ray spectra and their atomic numbers were shown to correspond to four places in the periodic table which previously had been vacant.

All the isotopes of an element have the same atomic number but different atomic weights. This is evident, of course, since there are only 92 atomic numbers (from hydrogen to uranium). It would be impossible, therefore, for the ten isotopes of tin (No. 50) to have different numbers. If ten different numbers for this element were possible, nine of these isotopes would be placed in groups where, because of physical and chemical properties, they evidently do not belong. Furthermore, the X-ray spectrum of an element which may consist of several isotopes settles this matter beyond any question. Each element, regardless of the number of its isotopes, gives but one spectrum and has, therefore, but one atomic number. Isotopes may have different numbers of neutrons in the nuclei of their atoms, but the number of protons is the same for all the isotopes of an element.

From a consideration of the atomic numbers of the elements and their periodic classification we can make one interesting and important conclusion. There is no periodicity or recurrence of nuclear charges as there is of physical and chemical properties. The properties vary from one element to the next through a period of the periodic system and then are repeated with slight differences for the elements of the next period. The nuclear charge, on the other hand, varies by one unit from one element to the next straight through the entire table. We must look, therefore, for some explanation of the periodic feature of the properties of elements in the structure of the atom outside of the nucleus. Here we should find recurrences of some structural feature which corresponds to the recurrence of properties among the elements.

10. Restatement of the Periodic Law

In the light of what has been said in the preceding section, the Periodic Law (page 223) should be restated as follows: *The properties of an element are a periodic function, not of its atomic weight, but of its atomic number.* This means that as we pass from one element to another in the periodic system,

the nuclear charge increases by one unit at a time. The charge of the nucleus depends upon the number of protons in it, and the change in nuclear charge shows that this number increases by one as we pass from one element to the one next following it. Thus, the hydrogen atom (atomic weight, 1.008) has a single proton in the nucleus. The nucleus of the helium atom contains two protons, but its mass is approximately four times the mass of a proton, it also contains two neutrons, since the element's atomic number is 2. The next element, lithium, exists in two isotopic atomic forms. These have masses of 6 and 7, respectively. The nuclei of both kinds of lithium atoms, however, have the same nuclear charge, since there is but one possible atomic number for the element. This number is 3. Hence, the nucleus of the atom of mass 6 contains three protons and three neutrons, the atom of mass 7 contains three protons and four neutrons. *The atoms of isotopes have different masses but the same nuclear charge.* Isotopes, therefore, have the same atomic number. Since the isotopes of an element are practically identical except for atomic weight, the dependence of the properties of an element upon atomic number rather than upon atomic weight is obvious. The periodic classification of the elements shown in the Periodic Table on the inside of the back cover of this book is based upon atomic numbers.

THE STRUCTURES OF CRYSTALS

11 Introduction

In determining the atomic numbers of the elements, Moseley used a crystal for which the spacing between atomic planes was known. From this distance and from the angles at which reflections of the different X-ray waves were obtained, he calculated the wave-lengths of X-rays originating in the atoms of different elements. Now this method can also be used to determine the

spacing between different sets of planes in a crystal, if a single (monochromatic) X-ray wave-length is employed, and if the crystal is rotated about some axis in order that the beam of X-rays will fall upon different sets of planes at the proper angle for reflection. Before attempting to describe the structures of crystals as determined by their diffraction of X-rays, let us describe briefly their external forms.

12. The Forms of Crystals

As already suggested we believe that the particles composing a crystal are arranged in orderly lines and planes. The external forms of crystals first indicated this to be true. Every crystal has a definite form which can be described in geometrical terms. It is bounded by plane surfaces called *faces*. These make characteristic angles with one another and are arranged in an orderly fashion with respect to certain lines which can be drawn through the crystal. These lines represent the crystal's *axes*. The axes of the crystal in Figure 114 are represented by the heavily shaded lines that are drawn perpendicularly to the faces of the cube.

Crystals are classified into six groups, depending upon the relative lengths and the arrangement of their axes. The six fundamental systems of crystals are shown in Figures 114-119, and are described below.

(1) Regular, cubic, or isometric system (Figure 114). These crystals have three axes of equal lengths at right angles to one another.

(2) Tetragonal system (Figure 115). These have three axes at right angles to one another, but with one axis of different length from the other two.

(3) Orthorhombic system (Figure 116). These have three axes, of which no two are of equal length, but all are at right angles to each other.

(4) Hexagonal system (Figure 117). These have four axes, three of which are in one plane and make angles of 60° at their point of intersection, and a fourth at right angles to these three.

(5) Monoclinic system (Figure 118). These have three axes of any relative lengths, one axis

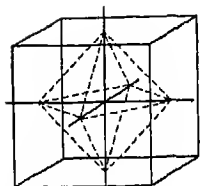


Figure 114 Regular System

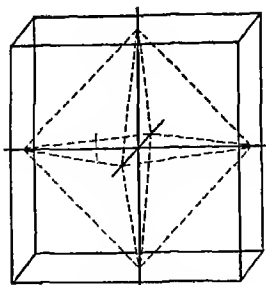


Figure 115 Tetragonal System

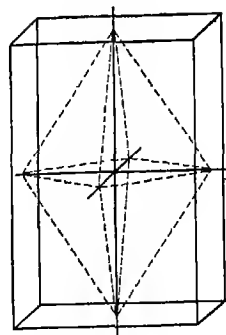


Figure 116 Orthorhombic System

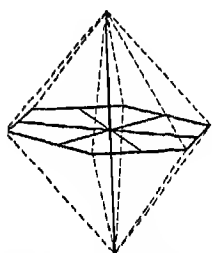


Figure 117. Hexagonal System

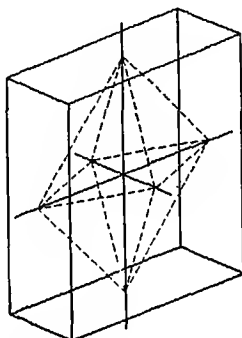


Figure 118 Monoclinic System

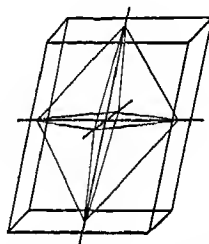


Figure 119 Triclinic System

is inclined at an angle of 0° – 90° to one of the other axes, but each of these is at right angles to the third

(6) Triclinic system (Figure 119) Three axes of these crystals have any relative lengths, and each axis is inclined toward the other two

The system to which the crystals of a given substance belong is as characteristic of that substance as its other properties. The shape and appearance of the crystal may vary, but these variations do not mean that the fundamental crystalline character is different for different exterior forms. Sodium chloride, for example, may crystallize as cubes or as octahedra (Figure 114), but both of these forms belong to the regular system of crystals. There are many different crystal-forms, but all of them can be properly classified in the six fundamental systems described above

Different substances that crystallize in the same system and form crystals that have axes of the same relative lengths and inclined at the same angles are said to be *isomorphous*. On the other hand, the same substance does not always crystallize in the same system. Carbon, for example, crystallizes as diamond in the regular system and as graphite in the hexagonal system. Sulfur forms both monoclinic and orthorhombic crystals. These modifications are called *allotropic* forms of the substance.

13 The Crystal Lattice as Determined by X-Rays

When a monochromatic (one wave-length) beam of X-rays falls upon the upper face (Figure 120) of a crystal of sodium chloride, the beam is reflected at a definite angle,

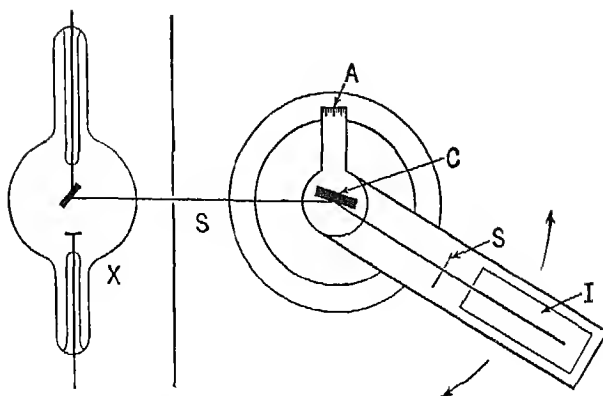


Figure 120 Apparatus Used to Study the Structures of Crystals by Means of X-Rays

The X-rays are produced in the tube X, pass through the slit S, and fall upon the crystal C. Here they are reflected by planes of atoms. The direction of the reflection is found by moving I through the arc of a circle around C. When it is in the correct position the reflected beam of X-rays enters I and ionizes the gas that it contains. The angle of reflection is then read on Scale A.

which can be measured. From the magnitude of this angle and the wave-length of the X-ray, the spacing of the planes parallel to this face can be determined. When the crystal is rotated about one axis, so that the beam becomes incident to another face like the first, reflection is obtained at exactly the same angle, indicating that the spacing between the planes parallel to this face is the same as that between the first set. A similar result is obtained each time the crystal is rotated through 90° about the same axis. If the crystal is rotated about some other axis, as for example the axis that may be

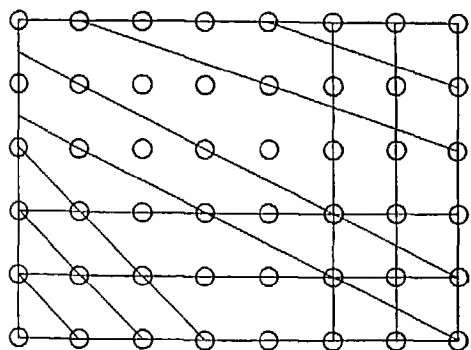


Figure 121 Some of the Sets of Planes in a Crystal that will Reflect a Beam of X-Rays

The planes of each set are separated by a definite distance between planes and, therefore, each set of planes will reflect the beam at a definite angle.

drawn from one corner of the cube diagonally through the cube to another corner, some other set of planes (Figure 121) may be made to reflect the beam. The magnitude of the angle at which this reflection is observed shows that the spacing is different, and from the magnitude of the angle the spacing can be determined. Information of this kind makes possible the assignment of definite positions to the atoms, or other particles, of which the crystal is composed. These positions lie at the points where the different atom-bearing planes of the crystal intersect. An orderly pattern of the particles arranged in three dimensional space is thus determined for a given crystalline substance. This pattern, or array, is called a *crystal lattice*, or it is sometimes called a *space lattice*. The smallest portion of the crystal that reveals the complete lattice pattern is called a *crystal unit*. For an illustration of what is meant by a crystal lattice, we may refer to Figure 125 or 126. In a sense, we may think of different lattices as different methods of piling spheres together, provided that it is correct to think of atoms or molecules as spheres.

The method described above for the study of crystalline substances was developed by W. H. Bragg and W. L. Bragg. An earlier

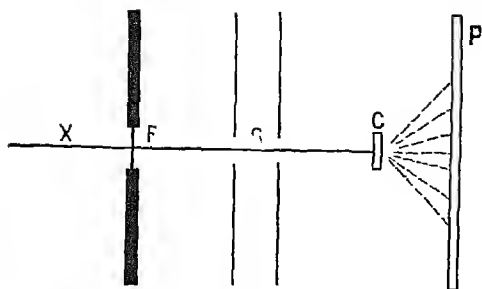


Figure 122 Laue's Method of Studying the Structures of Crystals

The beam of X-rays (X) strikes the crystal C and passes through it. In doing so it is diffracted by many sets of planes, each set causing a diffracted ray to strike at a different point on the plate (P).

method was suggested by Laue. By Laue's method a beam of X-rays is passed through a crystal and eventually strikes a photographic plate (Figure 122). Many different sets of planes diffract the X-ray beam, each set of parallel planes producing its own diffraction spots on the photographic plate. The distance and direction of the spots from the center depend upon the inclination of the planes with reference to the direction of the beam's path, and they depend, also, upon the spacing between parallel planes. The dark spots on the plate represent the different directions in which reinforcement of the beam occurs. The plate is not affected at other points, because interference destroys the X-rays in these directions. The symmetrical arrangement of spots in the photograph corresponds to a similar symmetry of planes within the crystal.

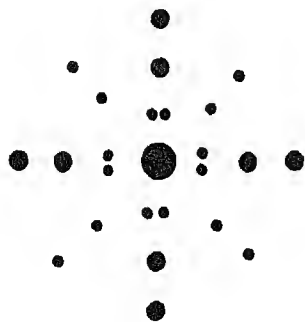


Figure 123 A Pattern of Spots Obtained on the Photographic Plate (P) of Figure 122

14. Crystal Structures

The structures of crystals of many metals, non-metallic elements, natural substances, and chemical compounds such as sodium chloride and magnesium oxide have been studied by the methods described above. Upon the basis of the kinds of particles that act as the structural units and the nature of the forces that bind the particles together, crystals may be classified as follows: (1) atomic, (2) molecular, (3) metallic, (4) ionic.

In *atomic crystals* single atoms are the units, and these are bound together by forces similar to those between the atoms of covalent compounds, i.e., by the sharing of electron pairs. Carbon forms crystals of this kind. *Molecular crystals*, as the name implies, consist of molecules of some element or compound held together by forces of the same nature as those which produce cohesion and attraction among the molecules of a liquid or a gas (page 100). Solid chlorine, Cl_2 , carbon dioxide, water, and many organic compounds form crystals of this kind. In general, metals form crystals in which the valence electrons of the atoms (page 58) are scattered throughout the crystal's structure and serve to bind the positively charged metallic ions together. Having lost their free, or valence, electrons, the metallic atoms of the crystal are positive ions rather than electrically neutral atoms. Crystals of this kind are called *metallic*.

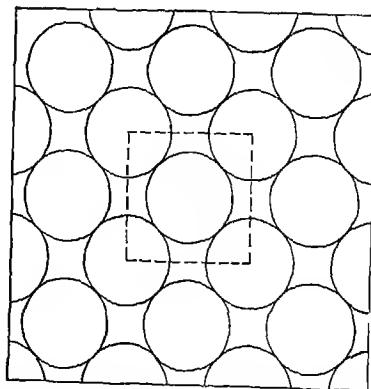


Figure 124 A Face-Centered Crystal Pattern, Showing the Packing of Atoms

crystals. *Ionic crystals* are illustrated by the crystals of sodium chloride, which are described below. These crystals are composed of ions arranged in many different geometrical forms, one of which is the lattice of sodium chloride

15. Types of Crystal Lattices

The atoms, molecules, or ions that compose the lattices of crystals are arranged in many different patterns, depending upon the size of the particles, their structures, and the nature of the valence forces that bind them together. A few of the different kinds of lattices are shown in the sketches on this and the following pages. Copper, silver, gold, and several other metals crystallize in a variety of the regular system called the *face-centered* lattice (Figure 124). This drawing represents the packing of atoms in a large crystal, the space lattice — or crystal unit — is indicated by dotted lines and is also shown in Figure 125. Most of the metals that are ductile and easily beaten or rolled into thin sheets crystallize in the face-centered lattice pattern. The malleability and ductility of metals depend, of course, upon the ease with which the atoms of their crystals can slip over one another under pressure. In crystals that are based upon the face-centered lattice, planes of atoms may slide or slip over and past other planes without actual fracture of the crystal. Magnesium, zinc, and certain other metals

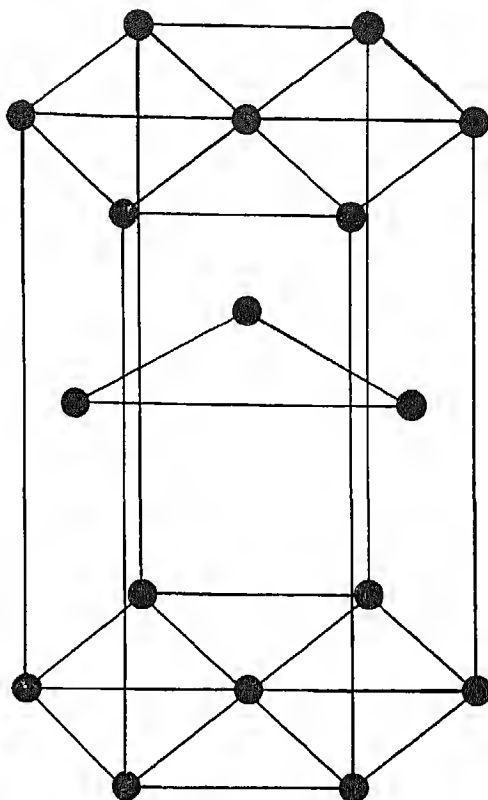


Figure 126 Hexagonal Lattice

form crystals based upon the *hexagonal* lattice (Figure 126). The face-centered and hexagonal lattices represent very close packing of atoms in crystals. Some metals, such as sodium and potassium, crystallize in the *body-centered* type of lattice (Figure 127), in which the packing of the atoms is

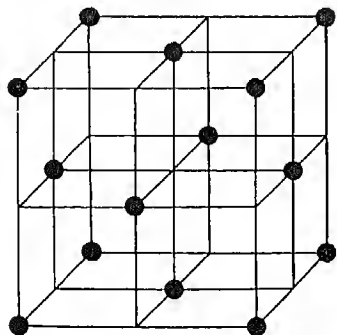


Figure 125 The Face-Centered Cubic Lattice

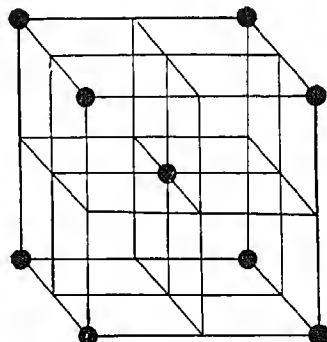


Figure 127. The Body-Centered Cubic Lattice

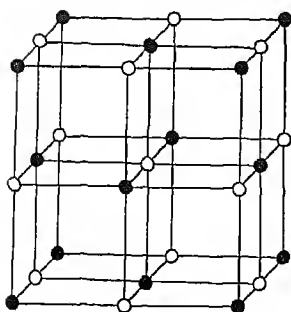


Figure 128 The Crystal Lattice of the Sodium Chloride Crystal

not so close or "tight" as it is in the face-centered and hexagonal types

16. The Structure of Crystals of Sodium Chloride

The pattern of the crystal lattice of sodium chloride is shown in Figure 128. The crystal unit is composed of eight small cubes, and the particles that make up the lattice are sodium and chloride ions. The sodium ion in the center of the large cube (Figure 128) is surrounded by six chloride ions, which lie at the centers of the six faces of the cube. In a large crystal each sodium and each chloride ion is the center of a similar cube.

The particles are held in more or less fixed positions in the lattice of the crystal by the electrostatic forces which the positively charged sodium ions and the negatively charged chloride ions exert upon each other. If the particles are given sufficient energy by the absorption of heat, for example, the forces which make possible the crystalline structure are overcome and the crystal melts. Then again, when salt dissolves in water, the structure vanishes because of the effect of the solvent in lessening the magnitude of the forces which hold the particles together. In the liquid salt and in solution, the forces of attraction and repulsion which are responsible for the pattern of the crystal still exist, but they have been considerably weakened by other effects such as thermal agitation or the influence of the solvent.

It will be observed that no one ion is combined with another of the opposite kind of charge in the crystal of sodium chloride.

This means that *there are no molecules* of this substance in the crystal. This statement is in keeping with our first discussion of sodium chloride and similar substances in Chapter 4. Not many years ago, however, the general opinion was that all compounds are composed of molecules, and even yet one frequently hears in the chemical laboratory, or reads in chemical literature, some statement about "molecules of sodium chloride." When so used, this expression refers to *one ion of each element*—a pair or set of ions—and is used to indicate the fact that in this compound the ions are present in equal numbers. There is very good evidence, however, of the existence of molecules of sodium chloride in the vapor, or gaseous, state of this substance.

Review Exercises

- How are X-rays produced?
- How are X-ray spectra of the elements produced?
- How are the atomic numbers of the elements determined from the X-ray spectra of the elements?
- In what respects is the periodic system of the elements based upon atomic numbers more satisfactory than the system based upon atomic weights?
- What evidence indicates that the atoms of isotopes contain the same number of protons in their nuclei?
- Which of the following statements are true?
 - Chlorine has two X-ray spectra because it consists of two isotopes.
 - Allotropic forms of an element crystallize in different systems.
 - Nuclei of atoms of isotopes contain the same number of neutrons.
 - X-rays have shorter wave-lengths than visible light.
- How are X-rays used to determine the structures of crystals?
- Explain space lattice, crystal unit.
- What are four types of crystal structures?
- What are the units, i.e., kinds of particles, of which each type of structure is composed?
- In what types of lattices do most metals crystallize?

12. Show by means of a sketch the arrangement of sodium and chloride ions in the crystal lattice of sodium chloride

13. What are isomorphous substances?

References for Further Reading

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RADIOACTIVITY

We may therefore conclude from these experiments that the phosphorescent substance in question emits radiations which penetrate paper that is opaque to light, and reduces silver salts

BECQUEREL

1 Introduction

Certain heavy elements display the peculiar behavior known as *radioactivity*. When these elements undergo radioactive changes, they are converted spontaneously into other elements, at the same time, certain other kinds of matter are liberated in the form of particles that can be identified because of differences in their masses, electrical charges, and velocities. Radioactivity therefore appears to involve the disintegration of certain kinds of atoms and should, for this reason, offer excellent opportunities for the study of the structure of matter. The particles liberated during the disintegration of atoms, for example, should throw some light upon the constitution of the atoms from which they come. Furthermore, the liberation of definite particles of matter during radioactive disintegration shows beyond serious doubt that matter does exist in the corpuscular state. This evidence goes a long way in proving the physical reality of the particles that we have only assumed to be real in developing the atomic and molecular theories of matter in earlier chapters. It is quite appropriate, therefore, that we should study radioactivity before taking up the detailed account of the theories of atomic structure and discussing the methods for obtaining the information upon which these theories have been based.

2. The Discovery of Radioactive Substances

In 1896, Becquerel found that uranium compounds emit penetrating rays. These rays were found to affect a protected photographic plate in much the same manner as X-rays. Becquerel also found that the rays cause the air through which they pass to become a conductor of electricity. This property was demonstrated by means of the electroscope, Figure 129. In a charged electroscope the gold leaf *A* and the insulated

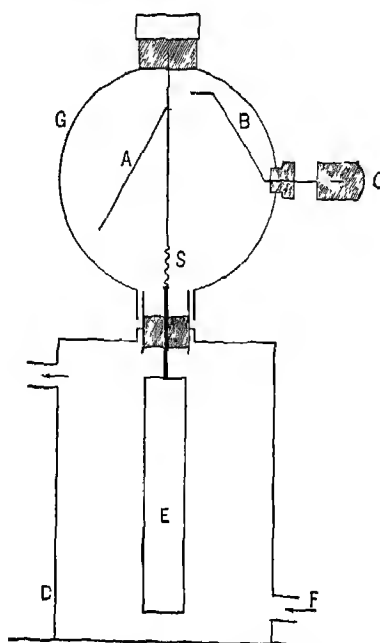


Figure 129. An Electroscope

support *S* are separated, because they carry like charges which repel. If air is passed over radioactive material and into *D* through *F*, the leaves fall together, showing that the electroscope loses its charge. The discharge occurs because the air that is subjected to the action of the rays is ionized, i.e., it is made a conductor of electricity and thus is able to remove the electric charge from the electroscope.

The rays from uranium compounds were found to differ from X-rays, however, in that they were not produced by any artificial means, such as the bombardment of the materials with streams of cathode-ray particles. Instead, they appeared to be emitted by certain materials quite spontaneously, at all times and under all conditions. The production of these rays, therefore, was a perfectly natural process. Further work showed that uranium minerals were more effective in producing the radiation than pure metallic uranium. The mineral *uraninite*, or pitchblende, which is composed chiefly of an oxide of uranium, was especially effective. Such facts indicated that these minerals contain one or more substances, besides uranium itself, that are active in producing the rays, and that these substances are more active than uranium. The task of discovering the character of these more active components of pitchblende was undertaken by Marie and Pierre Curie of France. After the death of her husband, Madame Curie carried on the investigation of radioactive materials alone. Because of her success she was twice awarded the Nobel prize, once with Becquerel and her husband, and once alone.

3. Radium

The task of the Curies consisted in separating the various substances in pitchblende. A ton of residues from the pitchblende mines of Joachimsthal was supplied by the Austrian government. This material was separated by chemical methods of analysis into seven portions. During all the work of separation, the activities of different portions were

closely checked and compared with those of other portions. For this purpose the rate at which an electroscope is discharged by the radiation produced by different substances proved an effective method of following the separations.

Eventually, two parts of the separated material were found to possess much more activity than the original material or any of the other portions. These two portions contained, respectively, the bismuth and barium of the original material. It was known, however, that neither bismuth nor barium possesses the ability to produce the rays. These results indicated, then, that the active elements were probably very much like bismuth and barium, since they had followed along with these elements during the chemical changes leading to the separations. In the bismuth fraction a new radioactive element was finally discovered and named *polonium*. The active element of the barium fraction was more difficult to isolate. Since it evidently resembled barium to a great extent, the barium was removed, as completely as possible, as barium chloride or bromide. Assuming that the active element was present in this material, as an impurity and in very small amounts, the barium salt was dissolved in water. The water was then allowed to evaporate until crystals were formed. It was thought that the chloride (or bromide) of the new element should be slightly less soluble than the barium compound. Furthermore, the use of the electroscope showed that the first crystals to form were more active than those that formed later. Hence, the first crystals were again dissolved, and the process was repeated over and over again. This method of separating two substances which differ in solubility is called *fractional crystallization*.

Finally, there was obtained about 0.2 g of a substance that could not be further separated by the method employed, and which, therefore, was judged to be pure. The metallic portion of this substance was found to be different from all other elements

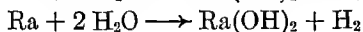
It differed from barium, which it most closely resembles, in its ability to produce the same kind of rays as uranium. It was evident, however, that it was not uranium, because its activity was much greater, the activity of the new substance was about one million times greater than that of the original material. The new element was named *radium*.

4. Production of Radium

Up to 1925, most of the radium produced in the world came from the mineral *carnotite* which was mined in Colorado and Utah. Some 150 tons of ore were required to produce one gram of radium, which was valued at \$100,000. In 1925, much richer ores were found in the Belgian Congo. More recently, Canada has become an important producer. Because of the greater yield from these sources the price of radium has dropped to about \$30,000 per gram. In 1940, radium was produced at the rate of about 100 g per year, and the total quantity produced up to that time amounted to about one kilogram, which in the form of radium salts is owned by university and industrial laboratories, hospitals, and clinics.

5. Properties and Uses of Radium

Chemically speaking, radium is not a very unusual element. It resembles barium, strontium, and calcium very closely. Thus, it has a valence of 2 in the chloride CaCl_2 , SrCl_2 , BaCl_2 , RaCl_2 . It also acts upon water in the same manner as these metals.



These properties were demonstrated by Madame Curie who first produced the pure element in 1910. She found its atomic weight to be 226.

Radium is interesting particularly because it emits rays similar to those first discovered in the case of uranium. This property has been named *radioactivity*. It is a property possessed, therefore, not by radium alone but by all *radioactive* substances, including uranium. There are many such substances, as we shall show later (page 250). The

radiation which they emit can be detected by the following methods:

(1) The rays emitted will pass through substances which are opaque to light rays, and can be detected by a photographic plate which is protected from the action of light.

(2) The rays will discharge an electroscope, since they cause the air through which they pass to become a conductor of electricity.

(3) The rays cause certain substances to phosphoresce or glow. Zinc sulfide is an example of a substance of this kind. Hence a screen coated with zinc sulfide can be used to detect the rays.

(4) A photograph of a space which is supersaturated with water vapor and which is exposed to the action of radium, or some other radioactive substance, reveals the actual path of the rays as straight lines. It is assumed that the rays cause the molecules in the space through which they pass to become electrically charged. If, for example, they cause a molecule or an atom to lose one or more electrons, a positively charged ion is produced. These charged particles then act as nuclei about which water condenses in small drops. The lines revealed by the photograph, therefore, are produced by these tiny droplets of water which form along the path of the ray.

The rays emitted possess energy as shown by their ability to affect the photographic plate, to cause zinc sulfide to emit light, and to render air a conductor of electricity. Furthermore, the emission of rays is attended by a liberation of heat, one gram of radium evolves 133 calories of heat per hour. These facts indicate that the radium atom is a source of energy that is released, in part, in some strange way during radioactive disintegration. Neither the change itself, nor the rate at which it occurs, is influenced by conditions which generally affect chemical action. Radioactivity is not influenced by any known catalysts, nor does it vary with changing temperature. It occurs at very low temperatures at the same rate as it does at very high temperatures.

Mixtures containing radium compounds are used in making luminous watch and clock dials and as coatings for articles, such as light switches,

that must be seen in the dark. For this purpose, zinc sulfide and some radium compound are mixed in a proportion of about 100,000 parts to 1. Dial figures made of, or containing, this phosphorescent mixture glow in the dark and therefore are visible.

Aside from purely scientific work involving the study of radium and its radiation, the best known use of the element and its compounds — RaCl_2 and RaSO_4 , are most often used — is in the treatment of malignant growths, such as cancers. The rays emitted by radium are said to destroy malignant tissues without injuring healthy, normal tissues of the body. This use is familiar to all and claims at least some measure of success in the fight of medicine and surgery against cancer. The use of radium appears to be most successful in the treatment of malignant growths on the surface of the body. Instead of radium compounds, radon (a radioactive element resulting from the disintegration of radium) is frequently used; this element is a gas. Powerful X-rays, instead of radioactive substances and their radiations, are also used in treating certain diseases.

6 The Kinds of Rays Emitted by Radioactive Substances

Following the discovery of radioactivity, great interest was displayed (1) in determining which elements are radioactive and (2) in the nature and effects of the radiations that they emit. We shall deal at this time with the second of these problems.

The earliest idea of the nature of the rays was that they are like X-rays and, hence, of the same nature as light. This idea was soon shown to be erroneous. For one thing, the rays were found to be non-homogeneous, i.e., they are composed of different varieties of rays. Three distinct varieties were detected, and further study showed that two of these varieties are not like light. Instead of being waves, or true rays, they were found to consist of rapidly moving *particles* of matter.

The three varieties of rays produced from a radioactive source may be separated in the manner shown in Figure 130. The radioactive substance is placed in a depression

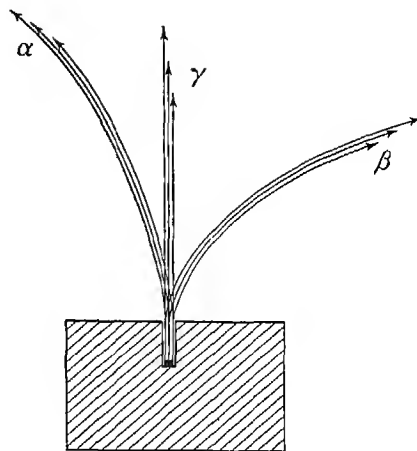


Figure 130. The Separation of Alpha, Beta, and Gamma Rays by Means of a Magnetic Field. The poles of the magnet are located at right angles to the plane of the rays.

made by boring a hole in a block of lead. Since lead absorbs all three kinds of rays, only those which are emitted in an upward direction emerge from the hole. A small pencil, or beam, of rays is secured in this manner. The beam is separated into its three components by being caused to pass through a magnetic field, which is produced by the poles of a powerful electromagnet. A photographic plate, properly protected from light, is placed above the block of lead and the electromagnet. The development of this plate reveals the points at which the rays strike it. The beam of rays is divided into three parts. One of these strikes the plate directly above the hole; this is not deflected. Two other fogged spots appear on the plate, and one of these is displaced to a greater distance than the other. These spots indicate that the beam is further divided into two parts which are deflected in opposite directions by the magnetic field. Since a beam of light is not deflected by a magnetic field in this manner, the two varieties of rays that are deflected cannot be of the same nature as light. Their deflections are similar to those that occur for a small, electrically charged particle of any kind that passes through a magnetic field. Their direction of

deflection depends upon the kind of charge, + or -, and the extent of deflection upon the strength of the magnetic field, the quantity of charge, the mass, and the velocity of the particle. It is reasonable to assume, therefore, that (1) the deflected rays are composed of charged particles and (2) they consist of two kinds of particles, because the magnetic field deflects some of them in one direction and the remainder in the opposite direction (Figure 130). The rays that are deflected most act as negatively charged particles, as indicated by the direction in which they are deflected, they are called *beta rays*, and the particles that compose them are *beta particles*. Those deflected to a lesser extent, and in the opposite direction, are *alpha rays* and are composed of *alpha particles*.

7. Alpha Rays

These are the least penetrating of all the rays emitted by radioactive substances. They are able to pass through a few centimeters of air or through a sheet of aluminum foil about 0.1 mm in thickness. The fact that these rays consist of particles can be demonstrated by means of a screen covered with a phosphorescent substance, such as

zinc sulfide. When such a screen is placed near a sample of radioactive material and observed by means of a microscope, the glow on the screen is seen to consist of numerous tiny flashes of light. The fact that the entire screen does not glow indicates that the rays that strike it are discontinuous in character. Apparently, each spot of light is produced by the impact of a single particle.

8 Fog-Tracks

The path of single alpha particles can be photographed by the method used by C. T. R. Wilson. A tiny bit of radium, or some other radioactive substance, is placed in a glass vessel containing air which is supersaturated with water vapor. To prevent the condensation of this vapor, the air must first be freed of dust particles, which act as nuclei upon which condensation occurs. When the air within the container is allowed to expand quickly into a region of greatly reduced pressure, it is cooled, and the water vapor condenses. General condensation does not occur, however. The particles which are emitted by the radioactive substance change the molecules of the gases in the air which lie along their paths into electrically charged particles (ions). These charged particles act as nuclei or centers of condensation. When a photograph is made while

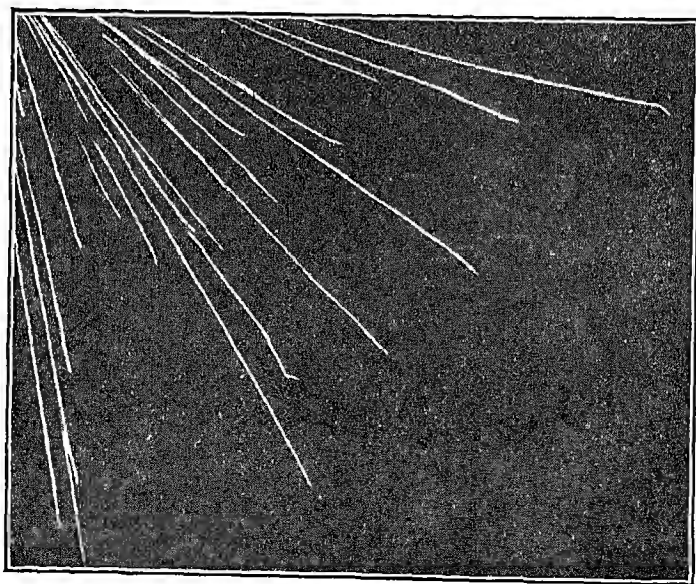


Figure 131. Fog-Tracks of Alpha Particles

these changes are occurring, the path of each alpha particle is revealed by the small drops of water which form on the ions, each of which becomes the center of a droplet. To obtain such a photograph, of course, the droplets must be properly illuminated. The path of a particle is usually referred to as a *fog-track*. The track of an alpha particle is revealed as a straight line. Sometimes a sharp deflection in the direction of the track is observed, usually near the end of the track, indicating that an impact with a molecule of the gas, or some part of such a particle, causes the alpha particle to suffer a change in direction. Naturally, such deflections most often occur when the alpha particle's energy has been almost completely exhausted by its passage through the an

9. What is the Alpha Particle?

The alpha particle has a positive electrical charge and acts, therefore, as a positive ion. This statement is based, at least in part, upon the fact that a beam or stream of these particles, when passed between two plates that are electrically charged -- one positively and the other negatively -- is deflected toward the negative plate in the same manner that a small steel ball possessing a positive charge is pulled toward the negative plate when it is rolled between the two plates. The deflection of the alpha particles in a magnetic field is also in the direction in which all positively charged particles are deflected when they move through such a field.

The deflection of particles by either the magnetic or electrical field depends upon several factors, such as the strength of the field and the charge, mass, and velocity of the particles. It is possible to calculate the mass and the charge of a single alpha particle when certain information is available concerning the strength of the field, the extent of the deflection, the number of particles emitted by a radioactive sample in a definite period of time, and the total charge of all the particles emitted. The mass of a single particle has been found to be 4, as compared with 16 for an atom of oxygen, on the scale of atomic weights. Since 4 is the

atomic weight of helium, the logical conclusion is that the alpha particle is an electrically charged atom of helium -- an ion of helium.

It should not be difficult to verify this conclusion. All that is necessary is proof that a sample consisting of alpha particles possesses the characteristic properties of helium. Since helium does not form compounds, it is not possible to base the comparison upon chemical properties. Helium can be detected, however, if it is made luminous (emits light). An electrical discharge through a tube containing helium under very low pressure produces light, which, when examined by the spectroscope, reveals a characteristic spectrum. When a small sample of radium is placed in a tube and all gases are then carefully pumped out, no spectrum is at first revealed by the spectroscope because there is no gas in the tube to become luminous under the effect of the electrical discharge. After several days, however, the spectrum of helium can be observed. Since the only possible source of helium is the sample of radium, the gas in the tube that produces the characteristic spectrum of helium must represent the alpha particles produced by the disintegration of radium atoms. The nature of the beta particles is sufficiently well known to prove that they could not be atoms of helium, and although another gas known as *radon* and closely resembling helium in some respects is found in the tube, it could not be responsible for the spectrum of helium. Radon was once called *niton*, it is one of the radioactive elements (page 250).

10. Beta Rays

These rays appear to consist of negatively charged particles. They are absorbed by sheets of aluminum of about 1 mm in thickness. They travel with much greater velocities, on the average, than alpha particles, and the velocity varies with the source of the particles. Sometimes it is almost as great as the velocity of light (186,000 miles per

second). These rays are deflected by electrical and magnetic fields, but in the opposite direction, of course, from the deflections of alpha rays. The mass of the beta particle is a little less than $1/1800$ of the mass of the hydrogen atom. It cannot be an atom of some unknown element, because there is no place for such an element in the periodic table. Furthermore, the beta particle does not act as an atom does in chemical changes, the change that occurs when a beta particle combines with an atom involves only the electrical charge of the atom — the atom becomes an ion. It is an *electron*, and although it acts as a particle of matter, it must also be looked upon as a unit of negative electrical charge, because all negative charges are multiples of its charge. Positive charges are also multiples of the electron's charge, but they differ in the "sign" or character of the charge. The electron is discussed further in the next chapter. It is now thought that beta particles are emitted during radioactive changes when neutrons are converted within an atomic nucleus into protons and electrons.

11. Gamma Rays

These are the most penetrating of the

rays emitted by radioactive substances, they pass through thin sheets of metals almost as readily as light passes through glass. Rays of the same properties are produced in the modern X-ray tube. The production of gamma rays by radioactive elements appears to be associated with the liberation of beta particles. It is possible that, in the disintegration of an atom of one of these elements, a neutron is converted into a proton and an electron, and that, at the same time, a definite quantity of energy is released as gamma radiation. It has also been suggested that gamma rays are produced when electrons and positrons (positive electrons) react and are converted into radiant energy.

12. Radioactive Elements

Radioactive change was explained by Soddy and Rutherford, in 1902, as a disintegration of atoms. This was a revolutionary idea, since atoms had been considered, since the time of Dalton, as the ultimate forms of matter. The evidence supporting Soddy's and Rutherford's explanation is so convincing, however, that there is little doubt of its correctness.

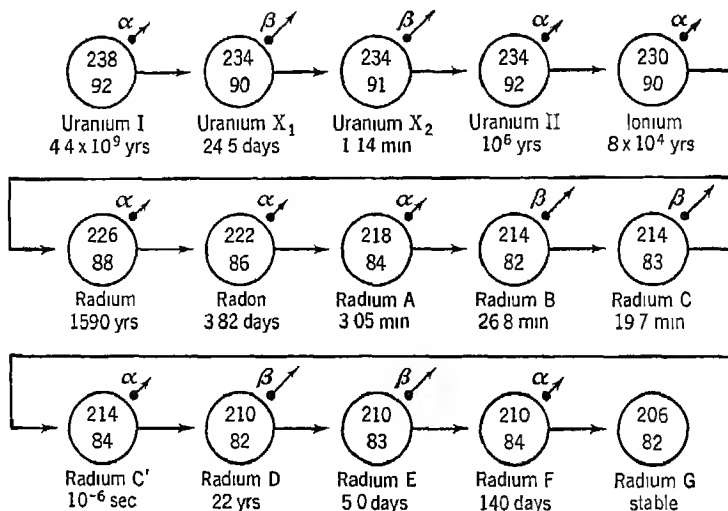


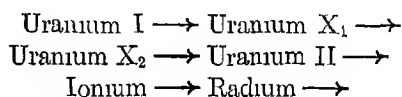
Figure 132 Transformation Series of the Uranium Family
(The upper number in each circle is the atomic mass, the lower, the atomic number. Below each circle is the name and the "half life" of the corresponding element.)

We have already stated that radon is produced at the same time that alpha particles are liberated by radium atoms. As far as we know, these are the only products of the radioactivity of this element, pure radium does not emit any beta particles. After a time, however, beta particles are produced, indicating that the radioactivity of radium produces other radioactive substances that do emit beta rays. The existence of these elements is proved by the deposition of metallic substances upon the walls of a vessel containing radon, which is of course a gas. These metals also are radioactive; they change from one element to another in much the same manner that radon is produced from radium. They cannot be separated or studied very easily, because they exist for only short periods of time. They are, however, produced continuously as long as the starting material lasts. Some information as to the number and nature of these substances can be obtained by observing the kinds of particles emitted and their velocities. Some elements emit alpha particles and some beta, and the speed of the particles and their range in air vary with the radioactive element producing them. Thus, the alpha particles emitted by the atoms of any one radioactive element possess the same maximum velocity. This is not true of the beta particles, although their velocity, in general, varies with their source, i.e., the average velocity of beta particles from one element is different from that of beta particles from another element. Hence, observation of the appearance of particles traveling from the radioactive source with a velocity different from that formerly observed, indicates the appearance of a new radioactive element.

All minerals that contain compounds of uranium also contain compounds of radium. In all these minerals the ratio of uranium to radium is constant — about 3,000,000 to 1. This ratio indicates that radium is produced from uranium at a very slow rate, if the change were rapid, all uranium would have

disappeared from the earth long ago. Furthermore, if all the radium is extracted from a mineral containing uranium, no appreciable quantity of radium is produced again within the lifetime of man. The radium that has accumulated in these minerals has been produced over a period of time that began when the minerals, or uranium itself, made their appearance as a part of the earth's crust.

Radium is not produced directly from uranium. A study of the particles emitted from minerals containing both of these elements indicates that there are four other radioactive elements between them; four other elements are produced before radium is formed.



In all, there are fourteen known radioactive elements in the series that begins with uranium and includes radium, Figure 132. If we start with a sample of pure Uranium I, some of its atoms change immediately, others are unchanged after a long period of time. The *average life* of an element refers to the average length of time that atoms of that element endure before they are changed into the next member of the series.

From an inspection of Table 9, one finds that most of the elements above radium decompose slowly, while those following it decompose very rapidly. The production and decomposition of radium is somewhat similar to the flow of water into and out of a reservoir. Radium may be compared to a reservoir into which water pours more slowly than it leaves. Hence only small quantities of the element can ever be present in the earth. In a given material, such as a sample of an ore of uranium, the different elements reach a state of radioactive equilibrium in which each is produced at the same rate as it decomposes. Let us compare the elements to a series of vessels arranged one above the other. Water flows into the top vessel at a constant rate. It leaves this vessel through a small opening at the bottom and flows into the next. The openings in the bottoms of the different vessels vary in size and, in this

TABLE 9

The Uranium Series of Radioactive Elements

Element	Periodic Family	Atomic Weight	Average Life	Half Life	Particle Emitted
Uranium I	6 A	238	6.43×10^8 yrs	4.4×10^9 yrs	α
Uranium X ₁	4 A	234	35 days	24.5 days	β
Uranium X ₂	5 A	234	17 min	1.14 min	β
Uranium II	6 A	234	4.3×10^5 yrs	2×10^6 yrs.	α
Ionium	4 A	230	2×10^5 yrs	8×10^4 yrs	α
Radium	2 A	226	2295 yrs	1590 yrs	α
Radon	0	222	5.6 days	3.82 days	α
Radium A	6 B	218	4 min	3.05 min	α
Radium B	4 B	214	38.5 min.	26.8 min	β
Radium C	5 B	214	28 min	19.7 min	β
Radium C'	6 B	214	1×10^{-6} sec	10^{-6} sec	α
Radium D	4 B	210	27 yrs.	22 yrs	β
Radium E	5 B	210	7 days	5 days	β
Radium F	6 B	210	202 days	140 days	α
Lead (Radium G)	4 B	206	—	—	—

respect, are comparable to the rates of decomposition of the different elements. After a time the water in each vessel will maintain a constant level. The quantity of water in any one vessel depends upon the size of the opening by which water leaves that vessel. Similarly with the radioactive elements, the quantity of a given element in radioactive equilibrium with the other elements of the series depends upon the rate at which the atoms of that element decompose. This rate is expressed as the average life or half-life period of the element. The *half life* of an element is the time required for one-half of a given weight of an element to undergo disintegration.

The average life of radium is only of moderate length. Its rate of decomposition is slow enough to permit an appreciable quantity of the element to be formed, and at the same time rapid enough to cause it to display pronounced and easily detected radioactive effects. It is for these reasons that radium is the best known of the radioactive elements.

In addition to the radioactive elements listed in Table 9, there are two other series, these are designated as the *actinium* and the *thorium* series. The disintegration in each of these series produces elements that, in general, correspond to members of the uranium series. In the actinium series, for example, actinium is produced instead of

radium, actinon instead of radon, actinium A instead of radium A, and so on. Hence all three series follow the same general course of disintegration.

13. Radioactivity and the Periodic System

Accepting the explanation of Soddy and Rutherford concerning the nature of radioactive change, one must conclude that the emission of either an alpha or a beta particle from an atom results in the production of a new kind of atom. Since the atomic weight of helium is 4, the loss of an alpha particle must mean a decrease of four units in atomic weight. Thus, the atomic weight of radium, as determined by Madame Curie, is 226. Since radon is produced from radium by the ejection of one alpha particle from an atom of radium, the atomic weight of radon should be 222. We may assume that radon is a monatomic gas, like all the well-known members of the series to which it belongs. The atomic weight might be determined, therefore, if the weight of a small volume of the gas could be measured. This determination, however, is difficult because only extremely small amounts can be obtained. Sir William Ramsay, in 1909, weighed a very small volume on a specially constructed balance and

calculated the weight of 22.4 liters (under standard conditions) as about 223 grams. Considering the sources of error and the difficulties involved, this value was very close to the expected result, 222. It appeared certain, at least, that the disintegration of the radium atom involved the ejection of only one alpha particle.

Let us refer to the list of radioactive elements of the uranium series on page 250. Assuming that one alpha particle is ejected at a time, it is observed that a total of eight particles is lost as an atom changes from uranium I to the end product (radium G). Since uranium has an atomic weight of 238, this means that the element at the end of the series should have an atomic weight of

$$238 - (8 \times 4) = 206$$

The element having an atomic weight nearest 206 is lead. Ordinary lead that is not associated with radioactive elements, however, has an atomic weight of 207.2. Richards was able to show that the atomic weight of the lead obtained from minerals containing uranium, and which might have been produced by radioactive changes, was always between 206 and 207 and approached 206. It appears, then, that the element at the end of the uranium series is lead. Although this element has a different atomic weight, its general properties are those of lead. Similarly, the lead that is associated with thorium has an atomic weight that is always greater than 207.2 and approaches 208. The changes in the thorium series from one element to another call for the loss of six alpha particles. Since the atomic weight of thorium is 232, the atomic weight of the element at the end of the series should be 208. Richards's results confirmed this expectation. Three kinds of inactive lead thus appear to exist in nature. Since all three have the same general properties, they must occupy the same position in the periodic system.

The ejection of a beta particle during the decomposition of an atom does not produce any change in atomic weight although a new kind of

atom is formed. The weight of the electron is a very small portion of the weight of the entire atom from which it is expelled. On the usual scale of atomic weights, its weight is only 0.00055 as compared to the atomic weight of oxygen as 16. The loss of this small mass by the atom of uranium X_1 , for example, means that the atom of uranium X_2 , which results, has an atomic weight of only 0.00055 of a unit less than that of uranium X_1 . Since this is a loss of only 0.00055 unit from a total mass of 234 units (the atomic weight of uranium X_1), it is beyond the limits of accuracy of the usual methods of determining atomic weights. As a matter of fact, there is no loss in mass at all. The ejection of the beta particle leaves the atom of uranium X_2 with a positive charge. If it endures long enough, it soon attracts and acquires an electron that enters its structure, thus, the atom of uranium X_1 becomes a *neutral* atom of uranium X_2 , which possesses a mass identical with that of the atom from which it was formed. The fact that a *different kind of atom* does result, however, indicates that the electron which is acquired enters a different portion of the atom's structure than that from which it was ejected.

The different elements of the uranium series occupy positions in different groups of the periodic system. Thus, uranium belongs to group six, radium to group two, radium B and radium D to group four, radon to the zero group, and so on. A study of Figure 133 reveals a very definite relationship between the shift from one group to another and the kind of particle emitted as this change occurs. It appears that the loss of an alpha particle shifts the position of the element back two groups in the periodic system. The ejection of beta particles produces an element that lies one group ahead of the element which undergoes the radioactive change. Thus, radium in group two loses an alpha particle and is changed to radon of the zero group. The atom of radium B (group four) loses a beta particle and is changed into an atom of radium C that belongs to group five. It thus becomes apparent that elements, such as radium B and radium C, which have *the same atomic weight*, do not necessarily

Group	III B	IV B	V B	VI B	VII B	O	I A	II A	III A	IV A	V A	VI A
Atomic Number →	81	82	83	84	85	86	87	88	89	90	91	92
Atomic Weight ↓												
238												U I
234										U X ₁	U X ₂	U II
232										Th		
230										Io		
228								Ms Th ₁	Ms Th ₂	Rd Th		
226								Ra				
224								Thx				
222						Ra Em						
220						Th Em						
218												
216												
214												
212												
210												
208												
206												

Figure 133 The Uranium and Thorium Series of Radioactive Elements and Their Positions in the Periodic Table

possess the same properties and do not fall into the same position in the periodic grouping of the elements. We have already pointed out, moreover, that there are three isotopes of lead. To these we may add radium B (atomic weight 214) and radium D (atomic weight 210), and also, corresponding elements of the actinium and thorium series (see page 252). All these elements exhibit the characteristic properties of lead, although they differ considerably in atomic weights.

14 Isotopes

Several groups of isotopes can be observed in Figure 133. These possess almost identical chemical properties but differ in atomic weight. Among such groups, the most prominent consists of the different elements in group four which possess the properties of lead and to which we have called attention in the preceding section. Another group consists of the three emanations, radon, thoron, and actinon, all of these are inert gases. In the periodic system all the elements of any

one of these groups must occupy the same position, i.e., they all fall in the same vertical group and the same horizontal row. For this reason, Soddy suggested that elements which possess the same chemical properties but have different atomic weights should be called *isotopes* (same position in the periodic table).

15. Radioactivity and Atomic Structure

Radioactivity is a property of certain elements, which in other respects closely resemble other elements and act in a perfectly natural manner both physically and chemically. Any light, therefore, which radioactivity throws upon atomic structure may be applied to the atoms of all kinds of elements.

Since radioactivity involves atomic decomposition, we must look for its explanation in conditions, within the atoms, which produce an unstable situation and which result in the ejection of certain parts of the atom in order that the parts remaining may

attain greater stability. All the facts that we know concerning radioactive changes indicate that the atom is composed of a number of structural units. We obtain direct evidence in favor of this idea when we observe the emission of alpha and beta particles from the atom. This leads to an entirely different picture of the atom than that provided by Dalton's atomic theory. Dalton pictured the atom as a compact, solid particle. It now appears that the atom is composed of several smaller particles, all of which are intimately related and arranged in a more or less stable group. Furthermore, the atoms of any one element do not contain necessarily the same number of particles, as shown by the fact that their masses may be different. This idea, too, is contrary to the earlier atomic theory, because Dalton assumed that all the atoms of any one element are exactly alike in every respect. The discovery of the isotopes of lead and of other elements proved this assumption to be erroneous.

Although it has shown that atoms are not what we once thought them to be, information concerning radioactivity has probably done more than any other one discovery to make atoms and molecules real to us. There can be no doubt that the forms of matter liberated during radioactive changes are corpuscular in character. The observation of the path of a single alpha particle in a photograph secured by Wilson's fog-track method, or of the tiny flash of light that the impact of the particle produces on a phosphorescent screen, is an observation of an atom of helium in action. The atom that produces the fog-track and causes the tiny flash of light is a physical reality. It is as real as an unseen bullet that leaves indisputable evidence of its existence when it strikes an obstruction in its path.

The discovery of the radioactive property of certain elements has had the following effects upon atomic theory:

(1) It has strengthened the atomic concept of

matter by demonstrating the physical reality of the corpuscles of which matter is composed.

(2) It has modified our concept of the atom by showing that the particles of the elements possess structure. They are not simple, compact bodies but are made up of smaller units of different kinds of matter.

(3) It has shown that all of the atoms of an element are not necessarily alike. In doing so it has revealed the error of Mendeleeff's periodic law by showing that the properties of an element are not periodic functions of the atomic weight. In fact it shows that the atomic weight of an element, in itself, has nothing to do with the properties of the element, since it is apparent that some elements with different atomic weights possess the same properties and that other elements of the same atomic weight possess different properties.

Because of such far-reaching effects upon our ideas of atoms and matter in general, the discovery and study of radioactivity has acted as a powerful influence in directing and encouraging investigations of the structure of the atom. As we have already shown, it was not even supposed that atoms possess structure until alpha and beta particles were recognized as disengaged parts of certain kinds of atomic systems. Naturally, the discovery of radioactivity and the properties of the radioactive elements encouraged attempts to liberate alpha and beta, or similar, particles from other atoms and to determine how they are arranged inside different kinds of atoms. If this could be done, it was hoped that the physical and chemical behavior of the atom could be explained. How successful these attempts proved and the discoveries to which they led will be the subjects of discussion in the next chapter.

Review Exercises

1. What changes in our ideas about atoms have resulted from the discovery of radioactivity?
2. What happens to an atom which undergoes radioactive disintegration?
3. What is the nature of each of the three kinds of radiation emitted by the radioactive elements?

- 4 How can alpha and beta particles be detected? How are they able to penetrate matter?
- 5 How do the positions (in the periodic table) of the elements which emit alpha particles differ from those resulting from the emission? Explain
- 6 Answer as in (5) for the elements which emit beta particles and the elements resulting from emission
- 7 What are isotopes? Explain the atomic weights of approximately 206 and 208 which some samples of lead possess. How should a value between 206 and 207 be interpreted?
- 8 What persons have been closely connected with the discovery, interpretation, and extension of our knowledge of radioactivity?
- 9 How is radioactivity different from ordinary physical changes? How is it like and how is it different from chemical changes? Should it be classified as a physical or as a chemical property?
- 10 If radium sells for \$30,000 per gram of metallic radium, what will 2 g of radium chloride, RaCl_2 , cost? Assume that the cost depends only upon the radium content
11. Approximately what weight of radium is con-

tained in a sample of ore that contains 1 g of uranium?

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THE STRUCTURE OF MATTER

To determine whether the metals be capable of being decomposed and composed is a grand object of true philosophy

SIR HUMPHRY DAVY

1. Introduction

We shall be concerned, primarily, in this chapter with such questions as the following: Are electrons, protons, and neutrons real? And if they are, what reasons can we find to justify our acceptance of their reality? What facts indicate that an atom has a nucleus, and that electrons move around it in orbits? How can we determine the numbers of electrons in the different groups or levels? In Chapter 4 we described the current views of atomic structure, but we did not attempt to answer these questions. We must now attempt to explain the evidence upon which theories of structure rest and the experimental methods that have been used in collecting this evidence.

Whatever ideas we may have concerning the structures of atoms must arise from deductions based upon the characteristic behavior, not of single atoms, but of observable quantities of different forms of matter. These deductions are somewhat similar to those that we might make if we were to watch the operation of a machine whose inner parts we could not see. We should observe the machine and its operation from all angles and under all possible conditions. We should attempt to determine what was going in and what was coming out of it. We should study the manner in which energy was being supplied to the machine, and carefully observe the action of every visible part of the mechanism for using or converting this energy. From our observations we

should select the most likely conclusion as to how the machine was put together and how it operated. If we wished to explain our conclusion to another person we should probably draw a picture or construct a model showing the parts of the machine in relation to one another. We have attempted to follow the same procedure with atoms, but the problem is somewhat different. We can at least see the machine, although we may not see inside it. If we were to use the most powerful microscope, the atom would still have to be greatly magnified before it could be seen. Nevertheless, we have tried to apply the same principles of mechanics to the atom that we apply to machines, and in keeping with these principles we have attempted to build models and to draw pictures of theoretical atoms by which the structure and behavior of real atoms can be explained.

In constructing atomic models our deductions concerning structures have been based upon observations, not of individual atoms, but of *matter in the bulk*. We have interpreted these observations, however, as depicting the behavior of *individual atoms*. Our sources of information include the following: (1) The chemical properties of different kinds of atoms, (2) physical properties, (3) radioactivity, (4) the periodic system, (5) the spectra of the elements, and (6) the effects of bombardments by alpha and beta particles. Thus, we can observe the wave-lengths (or colors) of light that atoms of a certain element emit and absorb, we can observe the particles that they eject if the element is radioactive; we can de-

termine their behavior when struck by rapidly moving particles; we can determine then chemical properties, such as valence, and their physical properties, such as density, boiling point, and solubility, and we can note the position that the element occupies in the periodic system. By reasoning back from effects to their causes, we can infer and deduce the character of the atomic structure that should give rise to the observed behavior. When this has been done, the usual procedure is to attempt to visualize all the parts of this structure and to set up a model that shows how these parts move, how they are related, and how they operate to produce the effects which we have observed. The models are based, of course, upon the ordinary system of mechanics, and it is only to be expected that such models should fail, perhaps not entirely, but certainly in some details. It is impossible to use ordinary measuring devices, such as stop watches and meter sticks, in determining the velocities and positions of different particles within the atom. If time and distance cannot be measured inside the atom, it is perhaps unwise to think of them as having any meaning. Ordinary mechanics requires us to use them, and consequently may be a somewhat unsound basis for deduction and interpretation of atomic phenomena. Developments in the field of atomic physics during recent years bear out this view and show that ordinary mechanics fails completely in dealing with many features of the behavior of atoms. It is not applicable, therefore, to atomic systems, although it is well suited to dealing with observable mechanisms. As a result, a new system of "atomic mechanics" is gradually replacing the old method of dealing with the problem.

Meantime, we must admit that no theory of atomic structure yet presented is adequate. The present is a time of changing points of view, of development. There is as yet no polished and universally accepted theory. The final outcome cannot now be foretold. Consequently, the views presented in this chapter are to be regarded as what are or have been considered good working hypotheses of atomic structure. The value of a theory, after all, lies in the stimulation and guidance which it provides for further search after the truth. The best of theories is destined to be outgrown, but in outgrowing it, man must come a little nearer the ultimate solution of the problem which the theory attempts to resolve.

THE ELECTRON

2. Cathode Rays

The beta particles emitted by the radioactive elements are electrons. Identical particles can also be liberated from other elements. We have no control over their emission by radioactive elements, but from other sources, the production of electrons can be brought about by artificial means and can be controlled. Treated in the proper manner, every element or any of its compounds, will liberate particles that are exactly identical with the beta particles emitted by a radioactive element.

One method often used to liberate electrons involves the use of the *cathode-ray tube*, Figure 134. Two wires, connected on the outside to a source of electrical potential (voltage), are sealed into the tube, which is evacuated by pumping out the air, or other gas, until the residual pressure is extremely low. Under these conditions, an electrical discharge occurs across the low-pressure space between the anode and cathode. During this discharge cathode rays are produced. These rays appear to travel in straight lines from the cathode, and cause the walls of the tube, where they strike, to glow. They can also be detected, or demonstrated, by placing a piece of metal foil in their path within the tube, the foil becomes hot if the rays strike it. They also cause a small pin-wheel to revolve, if such a device is placed in their path. A metallic object placed in the path of the rays casts a shadow upon the walls of the tube opposite the cathode. If a small pencil, or beam, of rays is selected by means of a slit in an obstruct-

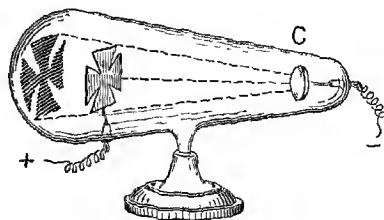


Figure 134 Cathode-Ray Tube

ing screen, this beam is deflected when it passes through a magnetic or an electrical field. The character of the deflection is the same as that suffered by any negatively charged particle in passing through such fields. In short, the properties of the cathode rays can be explained most satisfactorily by assuming that they consist of streams of extremely small negatively charged particles of matter.

3. The Mass and Charge of the Electron

The velocities of the particles composing cathode rays vary with the voltage between the terminals of the tube. Because of differences in velocity, different particles are deflected to different extents upon passing through magnetic and electrical fields. The deflection of a particle depends also upon its mass, its charge, and upon the strength of the electrical or magnetic field that deflects it. A particle which is uncharged is not deflected. A charged particle traveling with a high velocity will be deflected less strongly than one of the same mass and charge but which is traveling more slowly. For particles of different masses and different charges, but the same velocity, the most massive and the most lightly charged particles are deflected least. The situation is very much like that of a bullet fired from a gun in a direction parallel to the earth's surface. The deflecting field here is the gravitational field of the earth, which causes the bullet to describe a curved, rather than a straight path, and eventually to strike the earth.

Whatever mass the bullet has, the greater its velocity, the greater is the distance that it travels before it strikes the earth.

By observing the deflections of cathode-ray particles in electrical and magnetic fields of known strength, one should be able to arrive at some definite conclusions concerning their velocities, masses, and charges. Sir J. J. Thomson was thus able to determine the velocities of these particles. Knowing the velocity and the strengths of the deflecting fields, he was able to draw rather definite conclusions about the mass and charge of the cathode-ray particle. He did not determine the absolute values of the mass or the charge, he was able to determine only the ratio of the particle's charge, e , to its mass, m . He found that $e/m = 1.77 \times 10^7$ e.m.u. per gram. The abbreviation *e.m.u.* represents the *electromagnetic unit*, which is one of the units used by the physicist to express electrical charge.

To determine the absolute value of the mass, it would be necessary to know, or to determine, the value of the electron's charge, e . Now the ratio, e/m , for the charged atom (ion) of hydrogen is known. Whenever 1 gram-atomic weight ($m = 1.008$ g) of hydrogen is liberated by the electrical current, the quantity of electricity consumed is 96,540 units (called coulombs). This is used to neutralize the charges on all the hydrogen ions in one gram-atomic weight, and is therefore the quantity of electrical charge associated with this weight of hydrogen. Since 1 electromagnetic unit is equivalent to 10 coulombs, this charge amounts to 9654 e.m.u. for 1.008 g of hydrogen. This means then that the ratio e/m for hydrogen

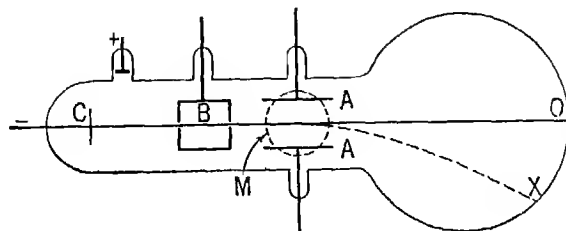


Figure 135 The Cathode-Ray Tube

Thomson used a tube of this kind to determine the ratio of the electron's charge to its mass. AA is the electrical field, M is the pole of a magnet, B is the slit system by which a pencil of rays is selected, O is the point at which the undeflected rays strike the walls of the tube, and X the point at which deflected rays strike. C is the cathode.

is 9654/1 008 Sir J J Thomson assumed that the hydrogen atom, when charged, possesses the same quantity of positive charge as the electron possesses of negative charge That is,

$$e \text{ (electron)} = e \text{ (hydrogen)}$$

$$e/m \text{ (electron)} = 1.77 \times 10^7 \text{ e m u per gram}$$

$$e/m \text{ (hydrogen)} = \frac{9654}{1\ 008} = 9578 \text{ e m u per gram}$$

Since the values of e are the same, the ratio of the mass of the hydrogen atom to the mass of the electron is $1.77 \times 10^7 / 9578$. Hence the mass of the hydrogen atom must be about 1845 times greater than the mass of the electron

4 Millikan's Determination of the Electronic Charge

Many attempts have been made to measure the charge of the electron. That of Millikan is probably most significant. He observed a droplet of a liquid between two electrically charged plates. When the plates were not charged, the droplet fell under the influence of gravity. When the plates were charged, the velocity of the drop was altered. Sometimes, it fell more rapidly, this meant, of course, that the charge on the drop was opposite (in sign) to the charge on the lower plate. Sometimes, the drop rose instead of falling, indicating that the charge on the droplet and that on the lower plate were of the same character, i.e., both were positive or both were negative. Electrons and positively charged particles were produced between the plates by means of a beam of

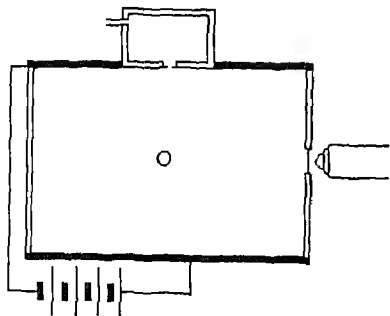


Figure 136 Millikan's Apparatus

The drop entered the space between the charged plates, from the small chamber above, through a tiny opening

X-rays. If the droplet absorbed an electron, when the lower plate was positively charged, its fall was accelerated. But if the lower plate was negatively charged, the velocity of its fall was decreased. If a sufficient number of electrons were absorbed to balance exactly the gravitational force, the droplet stood still. If a still greater number of electrons were absorbed, the droplet moved upward. In any event, the change in velocity produced by the absorption of the electrons or positive particles was proportional to the change in the charge absorbed.

Millikan found that all changes of velocity were multiples of a certain minimum change, which corresponded to the absorption of a unit charge. Other changes, therefore, were produced by the absorption of charges which were multiples of this unit. He thus demonstrated the "atomic" character of electrical charge as clearly as the law of multiple proportions reveals matter as acting in atomic quantities. By considering the velocity of the drop, its mass, the strength of the gravitational field and of the electrical field, and the viscosity of the air through which the drop moved, Millikan was able to calculate the quantities of charge on different drops. The smallest charge determined by these calculations represents the charge of the electron. This value was found to be 1.59×10^{-20} (electromagnetic units). Since the ratio of the electron's charge to its mass is known to be 1.77×10^7 , the electron's mass can be calculated. This turns out to be 9×10^{-28} gram.

A number so small as the mass of an electron can best be expressed by using negative exponents, e.g., 9×10^{-28} . This system is explained if we compare it with the well-known plan of writing large numbers as smaller numbers squared, cubed, etc. $10 \approx 1 \times 10$; $100 = 1 \times 10^2$, $1000 = 1 \times 10^3$, $700 = 7 \times 10^2$, $0.1 = 1 \times 10^{-1}$, $0.01 = 1 \times 10^{-2}$, $0.001 = 1 \times 10^{-3}$.

5 Avogadro's Number

We have already shown that the mass of

the hydrogen atom is 1845 times that of the electron. We can therefore calculate the mass of a single hydrogen atom as $1845 \times 9 \times 10^{-28}$ gram or 1.66×10^{-24} g. The value now accepted is 1.674×10^{-24} g. The weight of a molecule of hydrogen is twice this weight, or 3.348×10^{-24} g. The number of molecules of hydrogen in a gram-molecular weight is

$$\frac{2.016 \text{ g}}{3.348 \times 10^{-24} \text{ g}} = 6.02 \times 10^{23}$$

This is the number of molecules in a gram-molecular weight of any substance, and also the number of atoms in the gram-atomic weight of any element. The value of Avogadro's number that is now regarded as most nearly accurate is 6.0228×10^{23} .

6 Other Methods Used to Liberate Electrons from Matter

Electrons are emitted by certain metals, or their compounds, under the influence of heat. This may be spoken of as the thermal emission of electrons. Thus, the filament of the radio tube is heated by a current of electricity to a temperature at which it, or some material with which it is coated, emits electrons. These electrons stream across the space within the tube in the direction of the positively charged electrode, or plate, thus constituting a flow of current. This is similar to what happens when a current flows through a wire, in which electrons pass through the conductor, just as they flow through the evacuated region in the tube. But we are not to think of electrons as flowing through a wire as water flows through a pipe. Instead, we should think of them as passing from atom to atom. When electrons enter one end of the wire, others escape at the other end. The resistance of the wire is determined by the ease with which the atoms composing it allow electrons to be passed from one to the next.

Electrons are also emitted by the action of radiation of one kind or another upon elements or their compounds. Visible light

causes very active metals, such as sodium and potassium, to emit electrons. Ultra-violet light has the same effect upon certain other elements, while X-rays liberate electrons from all forms of matter. Electrons emitted in this manner are called *photo-electrons*. Other methods of liberating electrons from different forms of matter need not be discussed here.

Whatever their source or whatever the method by which they are liberated, electrons are identical. This fact, coupled with the fact that they can be liberated from any kind of atom, indicates beyond serious doubt that they are parts of all atoms. The problem of atomic structure, therefore, must deal with the number of electrons and their arrangement in the atoms of different kinds of elements.

PROTONS, NEUTRONS, AND POSITRONS

7. Protons

Since atoms are ordinarily electrically neutral, it is evident that there must be an electrically positive counterpart of the electron. On first thought we might conclude that this is the alpha particle, which carries a positive charge, and which is ejected from the atoms of certain radioactive elements. It is probably true that the alpha particle is one positively charged unit that is found in the structure of some atoms. It cannot be the smallest such particle, since its mass as compared to the mass (16) of an oxygen atom is 4, while the mass of the hydrogen atom is only 1.008. The hydrogen atom obviously cannot contain a positively charged structural unit which is more massive than the entire atom. The alpha particle, itself, must be complex in structure, as we have earlier suggested (page 50) and must be composed of smaller particles, some of which at least carry positive charges.

The fact that many atomic weights are whole numbers, or almost exactly whole

numbers, together with the fact that the atomic weights of the isotopes of other elements are also close to whole numbers (page 51), indicates that some particle with a relative mass of approximately 1, as compared with 16 for the oxygen atom, is a fundamental kind of particle from which all atoms are built up in nature. The only known particle having a mass of approximately 1 and a positive charge is the hydrogen ion, this particle, therefore, has come to be considered as one of the structural components of all atoms and has been given the name, *proton*. It will be remembered (page 50) that the hydrogen atom consists of one proton and one electron. If the electron is lost, as it is in the formation of a hydrogen ion, the proton is all that is left of the atom, the proton and the hydrogen ion refer to the same particle. Further evidence that protons exist in all atoms will now be given.

8. Positive Rays

The discovery of cathode rays encouraged attempts to find positive rays emanating from the anode. It was thought that these rays, if they exist, should travel in straight lines from the anode, and that in a tube, such as that of Figure 134, they should strike the cathode. If the cathode is perforated by a cylindrical opening, a pencil of positive rays should pass through the cathode into the region beyond. Here they may be studied without the interference of the cathode rays in the tube proper. Such rays have been observed. Their deflections in a magnetic or electrical field are in the opposite direction to the deflections of electrons in the same fields. For this reason, and also because they travel toward and through the cathode, the assumption that they are made up of positively charged particles appears to be justified. The opening in the cathode through which they pass is sometimes called a canal, and hence, the rays are spoken of as *canal rays*.

The particles of which positive rays are

composed are ions — positively charged atoms or even molecules. They do not emanate from the anode, as was first thought, but they are produced by impacts of cathode-ray particles, or electrons, with atoms and molecules of the gas in the tube, they vary, therefore, in charge and mass with the character of the gas. The smallest positively charged particle identified in positive rays is the hydrogen ion (proton), and here is further evidence that this particle may be the positively charged component of other atoms.

9. Protons as Units of Atomic Structure

The evidence which we have presented thus far does not necessarily convince one that all atoms contain protons. There is no doubt of the part played by the electron as a structural unit in the building up of atoms, but the part played by the proton needs verification. We must show, if possible, that hydrogen atoms, or hydrogen ions, actually exist in the structures of all other atoms. The best evidence that this is true is to be found in the results of the experiments described in the following section.

10. The Artificial Disintegration of Atoms

If atoms contain protons, it should be possible to liberate them if the atoms are decomposed. The emission of positively charged atoms of hydrogen would correspond to the emission of electrons and alpha particles by the radioactive elements. Rutherford and others, as long ago as 1919, decomposed atoms of nitrogen, aluminum, and other common elements by bombarding them with high-speed alpha particles from radium C or radium C'. When these alpha particles strike atoms and molecules placed in their path, other particles are produced. These are lighter than the alpha particles, and they travel for relatively long distances through the air or other substances before they are stopped. Hence they possess relatively large amounts of energy. In fact, their

energy appears to be greater than the energy of the alpha particles which produce them. The ranges of these particles are the same, or about the same, as the ranges of hydrogen atoms that are struck and driven forward when alpha particles are passed through pure hydrogen or through gaseous compounds of hydrogen. Furthermore, the ratio of the charge of one of these particles to its mass can be determined by the same method that Thomson used in determining the ratio of the electron's charge to its mass. The result confirms the conclusion that the particles liberated from nitrogen, aluminum, and other atoms are protons. These experiments, probably more than any other direct source of evidence, indicate that the electrically positive unit of the atom's structure is the proton.

11. The Neutron

When atoms of certain elements, such as beryllium or boron, are bombarded by alpha particles, uncharged particles called neutrons are emitted. They have a mass of about 1.00893 and a velocity that is about one-tenth that of light. These particles were first thought to consist of an electron and a proton in very close association and were sometimes referred to as electron-proton pairs. At present the general opinion is that the neutron is an independent, definite particle. Under certain conditions it may be made to disintegrate, whereupon it ejects an electron and becomes a proton. Since they carry no charges, neutrons can pene-

trate materials (even several feet of lead) much more effectively than electrons and protons, which are retarded by the charged particles of the atoms through which they pass.

12. The Nuclear Theory of Atomic Structure

The problem of the distribution of positive and negative charge within the atom has been the subject of many studies and has led to many answers. Sir J. J. Thomson pictured the atom as a sphere through which the positive charge was distributed. Here and there in this sphere of positive charge, the electrons lay much like "plums in a pudding." Thomson showed that the electrons would arrange themselves in concentric circles or groups within the positive sphere. The number of electrons in each group depended upon the size of the circle, being smallest for the circle next the center. This model of the atom, however, was not satisfactory. It failed to explain several points in the behavior of the atom. It failed particularly in explaining the results of the experiments described in the next paragraph.

In order to gain some information on this problem, Rutherford shot rapidly moving alpha particles through thin sheets of metals. He used, for example, a very thin gold foil. On one side of the foil he placed the radioactive substance which emitted the alpha particles, and on the other a phosphorescent screen. The latter was observed with a microscope, and the alpha particles striking within a certain area on the screen in a definite period of time were counted. Rutherford believed that an alpha particle which passed close to an electron in its passage through the foil would be only slightly deflected. Such deflections would not be sufficiently great to prevent the particle from striking the screen. If the alpha particle was greatly deflected, it would not strike the screen. He found that almost all the swift alpha particles which were emitted in the direction of the foil and screen were deflected, if at all, only slightly. This was

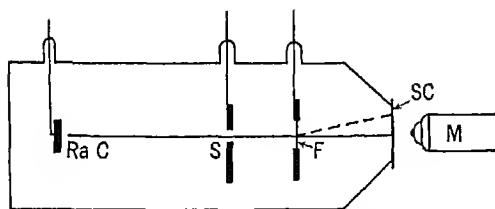


Figure 137 Rutherford's Apparatus Used in Studying the Deflections of Alpha Particles by Metallic Foils

The alpha particles were produced by Radium C and passed through the foil F, eventually striking the fluorescent screen SC, where they were observed with the aid of the microscope, M.

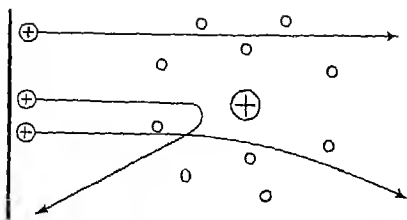


Figure 138 Deflections of Alpha Particles by an Atom

The large center circle represents the nucleus of an atom of metal in the foil. The small circles around it represent the planetary electrons.

indicated by the fact that approximately the same number struck the screen, when the foil of gold was placed in front of it, as when there was no obstruction. But now and then an alpha particle (one in many thousands) appeared to be deflected so strongly that it did not strike the screen at all, but was deflected through a large angle. In some instances, the particle was deflected backward towards its source.

Rutherford interpreted these results as meaning that the alpha particles usually met no deflecting forces, or very small forces such as might be exerted by electrons, in their passage through the space occupied by the atoms. This means, of course, that most of the space occupied by the atom is empty. As regards the positive charge of the atom, it means that the protons are collected in a very small space somewhere within the atom. This idea is supported by the fact that only rarely in its passage through the foil does an alpha particle meet, or pass near, a body which repels it very strongly. From the direction in which the alpha particle is deflected, it is obvious that the deflecting body carries a like (positive) charge. And from the extent of the deflection it is obvious that the alpha must approach, at times, very close to a deflecting particle, since the very great force which it evidently exerts could not be exerted at a very great distance. In short, it appears that the deflecting body acts almost as a positive charge located at a *point* would act.

Rutherford reasoned, therefore, that the positive charge of the atom (all the protons)

is located in a very small region at the center of the atom. He called this portion of the atom the *nucleus*. Since all the protons are located in the nucleus, it is from this source that alpha particles are emitted during the radioactive disintegration of certain atoms. Beta particles may also come from the nucleus. The protons and neutrons which are emitted by atoms under bombardment by swift alpha particles come from the same source. We know very little concerning the structure of the nucleus. The beta particles that are liberated may be produced by the disintegration of neutrons, in which case protons would be left in the nucleus.

13 The Composition of the Nucleus

At one time it was thought that the nucleus of the atom contained electrons and protons. The present opinion is that it contains only *protons* and *neutrons*. Since each proton or neutron has a mass of approximately 1 (as compared with 16 for the oxygen atom), the atomic weight if we neglect the small mass of the electron, is equal approximately to the number of protons and neutrons in the nucleus. The number of units of charge on the nucleus is equal to the number of protons. It is this charge that attracts electrons and holds them in their orbits. The number of these electrons is the same as the number of protons in the nucleus.

The nucleus of heavy hydrogen, or deuterium, contains one proton and one neutron, ordinary hydrogen has a single proton for a nucleus. The helium nucleus consists of two protons and two neutrons. The number of protons and neutrons combined in the nuclei of other atoms is equal to the whole number nearest the atomic weight of each element. The nuclei of isotopes differ only in the number of neutrons in their atomic nuclei.

14 Atomic Numbers

The quantity of charge on any nucleus is determined solely by the number of protons in that nucleus. Each proton contributes

one unit of positive charge and this is equal in size to the electron's charge. As we pass from one element to the next in the periodic table, protons are added one at a time, together with one or more neutrons. The nuclear charge increases, therefore, by one unit at a time, that of hydrogen is 1 and uranium is 92. This nuclear charge can be measured. By counting the alpha particles that pass through the foil and strike the screen in Rutherford's experiment, one can determine the number of alpha particles which pass through the gold foil without being deflected sufficiently to throw them off the screen. When the gold leaf is not in place, a similar count can be made of the particles which strike the screen in the same period of time. The difference between the two counts will be the number of particles that are deflected to a greater extent than a certain minimum angle. This number depends upon the size of the angle, the number of atoms in the foil, the charge on each atomic nucleus, and the charge, mass, and velocity of the alpha particle. Since the values of all the other factors are known or can be determined, the nuclear charge of the atom can be calculated.

The results obtained by the method described above showed that the number of units of positive charge on the nucleus of an atom is the same as the number which gives the position of the element in the periodic table. Long before Rutherford's measurements had been made, the number representing the position of an element in the periodic classification had been called the *atomic number* of that element. We may say, therefore, that the atomic number of an element is the same as the number of units of positive charge on the nuclei of its atoms. Atomic numbers are now determined by Moseley's X-ray method.

15. Positrons

The identification of the electron as a unit of negative charge led physicists to believe that there should be a corresponding

positive particle, a *positive electron*. The search for such particles was finally rewarded by their discovery among the products of certain atomic disintegrations. They have the same quantity of charge per particle as the electron, but the charge is positive instead of negative. Their mass is approximately equal also to the mass of electrons. Such particles are called *positrons*.

DISTRIBUTION OF THE ELECTRONS WITHIN THE ATOM

16. Introduction

In recent years, physicists and chemists have been most concerned with theories of nuclear structure, but earlier theories usually dealt with the arrangement of electrons about the nucleus. It is with the latter problem that we are concerned at this time. Instead of exact models (because it is not possible to determine at any one instant where all, or any, of the flying electrons of an atom are located), mathematical concepts and equations are most often used to express the facts that we know and the ideas that we have concerning the electrons' contribution to the structure of an atom.

Nevertheless, some models, although physically unreal, have been very useful, particularly to the chemist. Such models are very helpful in explaining, for example, the valences of different elements, and also in explaining how different atoms unite to form molecules. Although incapable of showing the actual atomic mechanism and its operation, these models represent — even in a physical sense — a fairly satisfactory, qualitative explanation of atomic structure. As such they have served to encourage and direct thousands of studies dealing with the structure of matter. For this reason, as well as for the aid which they offer in explaining chemical behavior, models of atomic structure are important. The first models employed by chemists were suggested in 1916 by Lewis, and later (1919) were extended and somewhat modified by Langmuir. These

have often been called static models, because the electrons were placed in definite positions about the nucleus rather than in orbits in which they rotated around the nucleus. For the most part, the theories of Lewis and Langmuir are now only of historical interest, although in earlier days they served as stimulating guides to study and research.

17 The Bohr Theory

Of the various atomic models which have been suggested from time to time, we shall confine our study to that proposed by Bohr. Aside from the purely mathematical methods of dealing with the problem of atomic structure, models based upon Bohr's theory are probably more nearly accurate and are certainly more helpful than any other.

Our present concept of the atom is based upon rather broad extensions of Bohr's original theory and pictures the atomic system as a miniature solar system. The nucleus is the sun and the electrons outside it are the planets. Like the planets of our solar system, these electrons are thought to rotate around their "sun." If they do not, the stability of the atom cannot be explained. If they rotate in orbits, they possess energy and are able to balance the pull, or attraction, of the positively charged nucleus, which tends always, of course, to draw them toward itself. If, in some way, they are given additional energy, the electrons may fly entirely beyond the usual boundaries of the atom, or if smaller amounts of energy are absorbed by the electrons, they may rotate in larger orbits, farther removed from the nucleus.

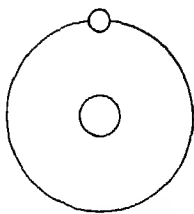


Figure 139 The Hydrogen Atom
Showing a proton in the center and the single planetary electron rotating in the orbit of smallest diameter

Under normal conditions, however, the attraction of the nucleus keeps them in rotation in what we may refer to as their "normal" orbits, that is, the smallest orbits that they can occupy within the atom.

18 The Hydrogen Atom and Its Energy Levels

The hydrogen atom consists of a single planetary electron revolving around the nucleus, which in this case is a single proton. The electron, however, may revolve in many orbits, depending on the energy which it possesses. Bohr's theory assumes that, as long as the electron rotates in the same orbit, it neither gains (absorbs) nor loses energy by emitting light. If it gains energy, the electron moves to a larger orbit. If it loses energy, it moves to an orbit of smaller radius.

Since the electron is a part of the atom, and since the electron possesses different quantities of energy when it revolves in different orbits, the *energy state* of the atom as a whole may be said to vary with the orbit occupied by the electron. Or putting the matter in another way, the different electron orbits may be said to represent different *energy levels*. If the electron lay in the nucleus, its energy would be zero, and this condition would represent the zero energy level. Hence, the orbit nearest the nucleus corresponds to the level of smallest energy and is called the first level.

19. The Spectrum of Hydrogen and the Origin of its Spectral Lines

Bohr's theory of the structure of the hydrogen atom, as briefly outlined above, was based largely upon the lines in the spectrum obtained by examination of the light emitted by the element when it is made luminous.

The hydrogen spectrum consists of four series of lines in the infrared, visible, and ultraviolet sections of the complete spectrum (page 234). Neither the infrared nor the ultraviolet rays can be seen by the eye, but they can be detected and studied by substituting for the eyepiece of the spectroscope a photographic plate that has been sensitized to these rays, thus allowing a

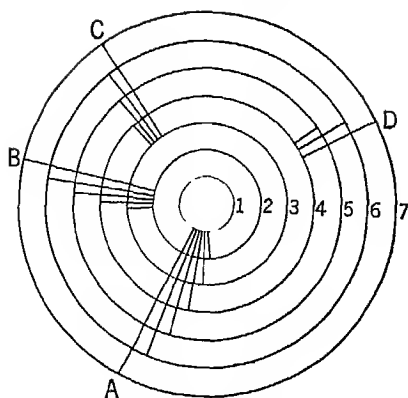


Figure 140 The Different Electron Orbits of the Hydrogen Atom

Four series of lines in the hydrogen spectrum are produced by the transition of electrons, from higher levels to the first (A series), to the second (B series), to the third (C series), and to the fourth (D series) orbits

photograph showing lines in these regions to be made

The frequency (velocity/wave-length) of any line in any of the four series of the hydrogen spectrum can be calculated by means of the following equation

$$v = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right),$$

where R is a constant for all of the lines, and n_1 and n_2 are integers. For one series, the Lyman, n_1 is 1 and n_2 is 2, 3, 4, 5, 6, etc. In the Balmer series n_1 is 2 and n_2 is 3, 4, 5, 6, etc. In the Paschen series n_1 is 3, and n_2 is 4, 5, 6, etc. In the fourth series, the Brackett, n_1 is 4 and n_2 is 5, 6, etc.

The Bohr theory of the atom offers at least a qualitative explanation of the four series and the individual lines of which each is composed (page 232). According to this theory, the electron of the hydrogen atom may revolve in any one of many orbits, and for each orbit there is a perfectly definite quantity of energy which the electron must possess to remain in that orbit. This energy depends principally upon the mass of the electron, its velocity, and its distance (the radius of its orbit) from the atomic nucleus, growing larger as the electron is farther removed from the nucleus. The orbits in which the electron can rotate are usually referred to by certain numbers, 1, 2, 3, 4, ... n . An electron in the first orbit possesses, therefore, the smallest quantity of energy that it can possibly have associated with it. Since all systems tend toward the lowest

possible energy state, this orbit is called the normal orbit for the electron. When hydrogen is acted upon by electrical energy in a discharge tube (page 233), we assume that electrons revolving in the first orbit of its atoms are forced out into larger orbits ($n > 1$) by absorbing energy. When this happens, electrons from outer orbits or from outside the atom may move back toward the nucleus, and revolve in orbits for which n has smaller values and in which they possess smaller quantities of energy. If the energy of an electron in the different orbits is represented by E_1 , E_2 , E_3 , etc., a quantity of energy equal to $E_2 - E_1$ must be radiated into space when the electron moves from the second to the first orbit. If the electron moves from the third to the first orbit, a quantity of energy equal to $E_3 - E_1$ is radiated, and so on. Each radiated quantity of energy corresponds to a definite frequency (ν), which is represented by a definite line in the spectrum of the element. All the lines corresponding to the frequencies of the radiation resulting from shifts of electrons to the first orbit make up, according to Bohr's theory, the Lyman series of the hydrogen spectrum.

Similarly, the lines of the Balmer series correspond to the frequencies of the radiation resulting from electron shifts from larger orbits to the second. The lines in the Paschen and Brackett series correspond to shifts of electrons to the third and fourth orbits, respectively.

Since the energy of an electron is smallest in the first orbit, transitions to this position result in the radiation of the largest quantities of energy. The frequencies of the radiation resulting from these transitions are therefore greater and the wave-lengths shorter than those corresponding to transitions to the second, third, or fourth orbits. The lines of the Lyman series lie, therefore, in the ultraviolet, and those of the Brackett series in the infrared. The visible lines belong to the Balmer series.

Not all of the series of lines in the spectrum of hydrogen were known at the time of Bohr's first statement of his theory of electron orbits. Bohr predicted the others and the frequencies to which their lines correspond with a high degree of accuracy.

20 The Distribution of Electrons in Different Levels of Atoms

We have already discussed the arrange-

ment of elections in different groups, or levels, about the nuclei of atoms of the first forty elements (page 54). The distribution for the heavier and more complex atoms is shown in Table 10, in which, for convenience, we have also summarized the distribution of electrons in the lighter atoms. The evidence upon which this distribution of electrons is based has been obtained from spectral data and from several other sources, a few of which are discussed briefly below.

21. The Structures of the Inert Gases

The numbers of elections in the atoms of the inert gases are evidently the numbers that are required to produce very stable arrangements, because these atoms are very stable. None of their elections can be removed without difficulty, and the atoms do not react by gaining, losing, or sharing any of the elections that they have. If the helium atom contains two elections in the first group, the neon atom must contain eight in the second group, because its atomic number, and therefore its total number of elections, is ten. Since the other inert gases are very similar to neon, we may reason that they also contain eight elections in the outermost groups of their atoms. If this is true, then it appears that the arrangement of elections in the different groups of their atoms is likely to be as follows:

Helium	2					
Neon	2	8				
Argon	2	8	8			
Krypton	2	8	18	8		
Xenon	2	8	18	18	8	
Radon	2	8	18	32	18	8

This plan gives us a general scheme of arrangement, a skeleton so to speak, that we can use in predicting the numbers of elections in the different groups of the atoms of other elements, as, for example, those that lie between neon and argon.

The atoms of the elements that follow immediately after any of the inert gases contain one

election that is relatively easily removed. Hence this election is believed to lie in the level next above the eight elections of the inert gas. The structure of the sodium atom may be represented as 2-8-1. The tendency of the sodium atom to lose *only* this single election is explained by the great stability of the atom that contains eight elections in the outermost group. On the other hand, the chlorine atom has the structure 2-8-7. It lacks one election of having the number required for maximum stability. It is difficult, therefore, to remove any of the seven elections of chlorine's outermost group. Instead, the atom tends to gain an election, thus completing the group and attaining an outer structure like that of argon.

After argon (2-8-8) the first two electrons go into the fourth level (K, 2-8-8-1 and Ca, 2-8-8-2). From scandium to copper, however, the additional elections are used to complete the third group, which is not filled until it contains eighteen elections (Se, 2-8-9-2, Cu, 2-8-18-1). For the next elements (zinc to bromine) elections are added to those already present in the fourth group, until in bromine this group like the corresponding groups in fluorine and chlorine contains seven elections (Zn, 2-8-18-2, Br, 2-8-18-7).

In krypton the fourth group contains eight elections, and hence, the next two that are added go into the fifth level (Rb, 2-8-18-8-1, Sr, 2-8-18-8-2). For the next elements (yttrium to silver) the elections that are added go to build up the fourth group from eight to eighteen (Y, 2-8-18-9-2, Ag, 2-8-18-18-1, Cd, 2-8-18-18-2). The fifth group is then built up until it contains seven elections in iodine and eight in xenon (I, 2-8-18-18-7, Xe, 2-8-18-18-8). In the next two elements (cesium and barium) the two elections that are added go into the sixth group (Cs, 2-8-18-18-8-1, Ba, 2-8-18-18-8-2). In lanthanum an election is added to the fifth group (La, 2-8-18-18-9-2) and then from cerium to lutetium the fourth level is built up from eighteen to thirty-two (Ce, 2-8-18-19-9-2, Lu, 2-8-18-32-9-2). The fourth group is now completely filled. From hafnium to gold the elections that are added build up the number in the fifth group to eighteen (Au, 2-8-18-32-18-1). The sixth group is then built up until it contains seven in element 85 and eight in radon (85, 2-8-18-32-18-7; Rn, 2-8-18-32-18-8): the next

Distribution of Electrons in Atoms

	Th	Pa	U	Np	Pu	Am	Cm
1	2	2	2	2	2	2	2
2	8	8	8	8	8	8	8
3	18	18	18	18	18	18	18
4	32	32	32	32	32	32	32
5	19	20	21	22	23	24	25
6	9	9	9	9	9	9	9
7	2	2	2	2	2	2	2

two electrons then go into group seven (Ra, 2-8-18-32-18-8-2) and in the last few elements (actinium to curium the electrons go to build up the fifth group from 18 in actinium to 25 in curium (Table 10)

22 Ionization Potentials of the Elements

The ionization potential of an element represents the strength of the electric field in volts per centimeter required to remove the most loosely bound electron from an atom of the element in its gaseous state. The ionization potentials of most of the elements are shown in Figure 141. It will be noted that the potentials required to remove one electron from an atom of each of the inert gases are relatively very high, and that it is small for each element following an inert gas in the order of atomic numbers. Thus, the potentials of lithium and sodium are both about five volts, while for helium and neon they are 20-25 volts. Beginning with lithium, the voltage required to remove an electron from an atom increases gradually until it reaches a maximum again for neon. There is a sudden decrease at this point to another minimum potential for sodium, followed by another series of increases until argon is reached. For potassium the potential again drops to a minimum, somewhat below the ionization potential for sodium. From calcium to zinc there is only a slight change in the potential, but from zinc to

krypton there is another series of gradual increases, with another maximum for krypton, followed by another sudden drop to a minimum for rubidium.

The ionization potentials of the elements, therefore, support in every way the arrangement of electrons that we have previously described. The energy required to remove an electron from an atom depends upon the nuclear charge, and as the charge increases, for example from lithium to neon, the ionizing potential increases. Another factor enters the picture and dominates the situation in the case of sodium. The nuclear charge is greater than for any of the elements from lithium to neon, but the electron is far easier to remove, and hence we must conclude that in the atom of sodium the electron that is removed must be farther from the nucleus than any of the electrons in atoms of elements below sodium. Evidently, then, all the electrons that are added one by one in the atoms of the elements from lithium to neon are approximately equally distant from the nucleus. This group must consequently contain eight electrons.

By similar reasoning we can determine the numbers of electrons in other groups. It is also possible to obtain additional useful information by measuring the ionization potentials required to remove another electron, and even two or three more electrons, from the atom after the first step in the

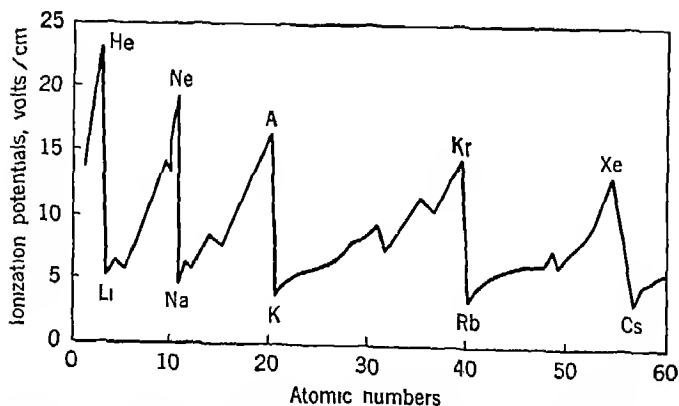


Figure 141. The Ionization Potentials of the Elements in their Gaseous States

ionization has been completed by removing the most loosely bound electron.

23. Atomic and Ionic Radii

Evidence supporting the theory of electron distribution in the different groups or levels of the atom can be found in the data dealing with the sizes of atoms and ions. Such data are given in Table 11.

Note that the radii of the atoms decrease for the elements in period two from lithium to fluorine and in period three from sodium to chlorine. As the charge of the nucleus increases it draws closer to itself the electrons in the groups around it, and electrons become increasingly difficult to remove. Note the increases in size for each of the group-one metals, lithium, sodium, potassium, rubidium, and cesium. It is in their atoms that a new group is started. Note, also, that their atoms increase gradually in size from lithium to cesium. The valence electron is most easily removed from the largest of these atoms, cesium, thus element, therefore, is most active and most readily forms positive ions, Cs^+ . Note, also, the increase in size of atoms of fluorine, chlorine, bromine, and iodine. The iodine atom is the largest of these, and hence it has the weakest attraction for electrons, and is least active as a non-metal. Note, finally, that for the transitional elements in the middle of the first long period (4) — vanadium to nickel — the radii are all of about the same size. In the atoms of these elements the electrons that are added go to complete the third group, and each contains the same number (2) in the group on the outside, hence there should be no great differences in the size of these atoms. From copper to bromine the fourth group is being built up from one to seven electrons, here, too, little change in size is to be noticed, except for a slight, gradual decrease as the nuclear charge increases.

Upon the basis of the sizes of their atoms, differences in the properties of the elements of a family are readily explained. Cesium, for example, has larger atoms than sodium (see atomic radii, Table 11, and hence the single electron in the valence shell of the cesium atom is more easily removed than the electron of the sodium atom, because it is farther away from the nucleus and is held less firmly. Cesium, therefore, is more

TABLE 11

Radii of Atoms and Ions

(in Angstrom units. One unit equals one hundred-millionth of one centimeter)

Element	Atomic radius	Ionic radius
Hydrogen	0.37	1.36, H^-
Lithium	1.50	0.68, Li^+
Beryllium	1.112	0.39, Be^{++}
Boron	0.7	0.24, B^{+++}
Carbon	0.77	—
Nitrogen	0.53	1.71, $\text{N}^=$
Oxygen	—	1.40, $\text{O}^=$
Fluorine	0.68	1.33, F^-
Neon	1.60	—
Sodium	1.86	0.98, Na^+
Magnesium	1.595	0.71, Mg^{++}
Aluminum	1.48	0.55, Al^{+++}
Silicon	1.172	0.44, Si^{++++}
Phosphorus	1.08	2.12, $\text{P}^=$
Sulfur	1.06	1.85, $\text{S}^=$
Chlorine	0.97	1.81, Cl^-
Argon	1.91	—
Potassium	2.27	1.33, K^+
Calcium	1.97	0.98, Ca^{++}
Titanium	1.45	0.62, Ti^{++++}
Vanadium	1.313	0.59, V^{++++}
Chromium	1.246	0.65, Cr^{++++}
Manganese	1.24	0.91, Mn^{++}
Iron	1.238	0.83, Fe^{++}
Cobalt	1.25	0.82, Co^{++}
Nickel	1.24	0.78, Ni^{++}
Copper	1.275	0.96, Cu^+
Zinc	1.33	0.74, Zn^{++}
Gallium	1.22	0.62, Ga^{+++}
Germanium	1.22	0.53, Ge^{++++}
Arsenic	1.25	2.22, $\text{As}^=$
Selenium	1.16	1.96, $\text{Se}^=$
Bromine	1.13	1.96, Br^-
Krypton	2.0	—
Rubidium	2.43	1.48, Rb^+
Strontium	2.14	1.15, Sr^{++}
Iodine	1.35	2.19, I^-
Xenon	2.2	—
Cesium	2.62	1.67, Cs^+
Barium	2.17	1.31, Ba^{++}

active than sodium in reacting with chlorine and other elements whose atoms can acquire electrons.

On the other hand, fluorine and chlorine are more active than iodine because their atoms are smaller than iodine atoms. The small atom of fluorine, for example, attracts very strongly and holds very firmly the electron it needs to complete its outermost shell, because this shell is close to

the nucleus. In the iodine atom, the additional electron must go into a group which is relatively far away from the nucleus and is held less firmly. When the atoms have acquired electrons and have become negatively charged ions, F^- , Cl^- , I^- , the iodide ion parts with its additional electron rather easily and, therefore, is readily oxidized back to the free element. The fluoride and chloride ions are more difficult to oxidize, because the electrons they have acquired are more firmly held. Similarly, the elements of the nitrogen family (nitrogen to bismuth) become more like the metals as the atomic weight and atomic number increase, because in the larger atoms, e.g., bismuth, the electrons are held less firmly, electrons are thus more easily removed, and the atoms may give up at least some of their valence electrons and act as metals do in forming positively charged ions, such as Bi^{3+} and Sb^{3+} . The other elements of this family do not form such ions, they form compounds by sharing electrons.

24. Some Factors that Determine the Type of Bond that Atoms Form

From left to right in one of the periods of the Periodic Table, the elements have increasingly greater ionization potentials (i.e., more and more energy is required to remove an electron from an atom), and increasingly smaller atomic and ionic radii (i.e., the atoms of successive elements have larger nuclei containing more protons which draw and hold closer to themselves the different electron-groups of the atom). Thus, the sodium atom of group one in the third period has little attraction for its single valence electron, and this electron is relatively far removed from the nucleus. Sodium, therefore, easily loses its valence electron to chlorine, for example, and thus forms sodium chloride, an ionic compound. Magnesium chloride likewise is ionic. In aluminum chloride, however, we find a compound which, in its pure state, displays many of the properties of covalent compounds. The high ionization potential of aluminum, and its small atomic radius, as compared with sodium, would lead us to expect that the atom of aluminum would have considerable attraction for elec-

trons, and evidently this attraction is strong enough to cause aluminum to share electrons with chlorine instead of giving them up completely. In carbon tetrachloride, CCl_4 , the positive charge of the nucleus is still greater, the atomic radius still smaller, and the tendency to yield electrons to chlorine still weaker for carbon than it is for aluminum. Although the aluminum ion, Al^{+++} , is formed and does exist as a hydrated ion — combined with molecules of water — in aqueous solutions, the carbon ion, C^{++++} , is unknown.

We see, therefore, that the type of bond — ionic or covalent — that the atoms of an element are likely to form depends upon the energy, as measured by the ionization potential, required to remove electrons from the atoms. This energy, in turn, depends upon the size of the atom, as measured by the atomic radius, and upon the positive charge of the nucleus. The formation of ionic bonds by positive elements, especially the metals, is favored by large atomic radii and small nuclear charges. The type of bond also depends, of course, upon the attraction that the atoms of the more non-metallie of the two combining elements have for electrons, and hence we might expect chlorine to form ionic compounds, whereas nitrogen or phosphorus or carbon might form covalent compounds with the same element.

25. Variable Valence Numbers of the Transition Elements

The iron atom in group eight possesses a positive valence in its compounds and appears to lose electrons, since it forms positive ferric and ferrous ions ($Fe^{+++}Cl_3^-$ and $Fe^{++}Cl_2^-$). This atom contains eight more electrons than argon, but it does not lose eight electrons. There are probably only two or three electrons in the *outermost* group of its atoms (Table 10). This condition is also true, in general, of many of the *d* elements of the long periods of the periodic table (the transition elements, such as chromium and manganese (see Table 10, page 269).

If the outermost group of the non atom contains only two electrons (Table 10), then when this atom has a valence number of 3, an electron from the next lower group must be released when the ferric (Fe^{+++}) ion is produced. It appears that a similar change occurs in many of the elements that have variable positive valences— Cu^+ , Cu^{++} , Mn^{++} , Mn^{+++} , Cr^{++} , Cr^{+++} , etc. Losses of electrons from an inside group can occur only when that group is not stable, or filled, thus, in the sodium atom the group next to the one on the outside contains eight electrons and consequently does not lose any. The sodium atom, therefore, never has any valence number other than +1.

Review Exercises

- What are some of the sources of evidence upon which theories of atomic structure are based?
- Describe a cathode-ray tube. What facts concerning cathode rays indicate that they are composed of negatively charged particles?
- By what method did Thomson determine the mass and charge of the cathode-ray particle?
- How did Millikan demonstrate the "atomic" character of electrical charge? How did he determine the unit of charge?
- What are some of the methods by which electrons can be liberated from different forms of matter?
- What is a proton? What is the relation of a proton to the hydrogen atom?
- Of what are positive "rays" composed and how are they produced?
- How are non-radioactive atoms disintegrated? What are the products of the disintegration?
- What is a neutron? How are neutrons liberated from atoms?
- Upon what evidence is the nuclear theory of the atom based? What is the composition of the nucleus? How do the nuclei of different kinds of atoms differ?
- Describe the structure of an atom of hydrogen according to Bohr's theory.
- What is the arrangement of electrons in each of the first nineteen elements of the periodic table?
- Why do we believe that the maximum number of electrons in the first group of orbits is two, and in the second, eight?
- How does Bohr's theory of atomic structure explain the radiation of energy by an atom?
- How does this theory account for the fact that some of the radiation by atoms of hydrogen is in the region of visible light and some in the region of the ultraviolet?
- What changes occur in the structures and electrical condition of atoms of sodium and chlorine when they react? Why does an atom of magnesium react with one of sulfur but with two of chlorine?
- Describe the atoms of the following elements as to (1) number of electrons in each group, (2) number of protons in the nucleus, (3) atomic number, and (4) maximum positive and negative electrovalence numbers of the elements aluminum, sulfur, fluorine, calcium, and zinc.
- What information concerning the atomic structures of different elements can be obtained from ionization potentials?

References for Further Reading

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ATOMIC NUCLEI AND ISOTOPES

A small amount of matter, the product of a chain of huge, specially constructed industrial plants, was made to release the energy of the universe locked up within the atom from the beginning of time

WAR DEPARTMENT RELEASE ON NEW MEXICO
TEST OF ATOMIC BOMB, JULY 16, 1945

1. Introduction

In this chapter, we shall be concerned, primarily, with the composition of atomic nuclei and with the changes by which nuclei of one variety of atoms are converted into the nuclei of other atoms. Isotopes are also discussed at this time because (1) the atoms of the isotopes of one element differ only in the composition of their nuclei, and (2) some knowledge of the subject is required for an understanding of the changes that occur in the transmutation processes by which one variety of atom is converted into one or more other varieties.

ISOTOPES

Previously (page 51) we have defined isotopes and explained the differences in the structures of their atoms. We now turn our attention to the experimental methods used to identify the different isotopes of an element and to determine their relative masses.

The belief that there is but one kind of atom for most elements persisted in chemistry even after the discovery of the isotopes of lead and other elements of the radioactive series. It was thought, for no good reason, that only elements associated in some way with the phenomenon of radioactivity exist in isotopic atomic forms. The correction of this view and the discovery of the isotopes

of non-radioactive elements came about as a result of Sir J. J. Thomson's studies of positive-ray particles.

2 Positive-Ray Analysis

The particles composing positive rays are electrically charged atoms and molecules, or *ions*, and their masses and charges vary, therefore, with the character of the small amount of gas in the tube. They are produced by the effects of cathode-ray particles (or electrons) upon atoms and molecules of this gas; the impacts result in the expulsion of one or more electrons and the production of positively charged ions. Positively charged particles produced in the region between the anode and cathode of a tube like that shown in Figure 142 move under the influence of a difference of potential toward the cathode. If the cathode is perforated by a small opening, a pencil of rays will pour through it and can be detected and studied in the region beyond. See Figure 142.

Using Sir J. J. Thomson's procedure, let us consider the positive particles produced in a discharge tube under the influence of a difference in potential of some thirty or forty thousand volts. After passing through the cathode of such a tube, the positive particles are deflected by being passed through an electrical and a magnetic field and finally allowed to strike the screen or photographic

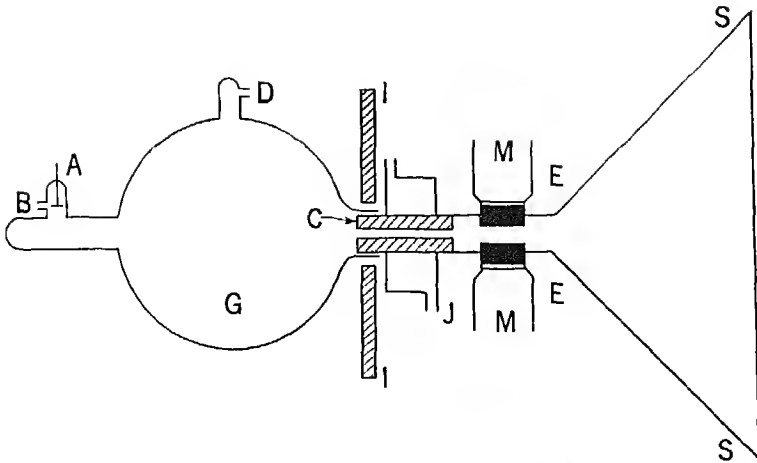


Figure 142 Thomson's Positive-Ray Tube

Positive particles originate in G and pass through the opening in the cathode C into the electrical field (EE) and magnetic field (MM). J is a cooling jacket through which cold water flows. I is an iron shield to prevent positive particles in G from being deflected by the magnet.

plate, SS. The electrical field alone causes particles of the same mass and charge, or particles having the same ratio of charge to mass, e/m , to be deflected along the line $E-E$ (Figure 143), the exact point at which each particle strikes being determined by the velocity of the individual particle. The magnetic field deflects the particles in circular paths which lie in a plane perpendicular to the field and also to the direction of the electrical deflection. This field when acting alone, therefore, will deflect similar particles along the line $M-M$ at points where the circular paths intersect the screen.

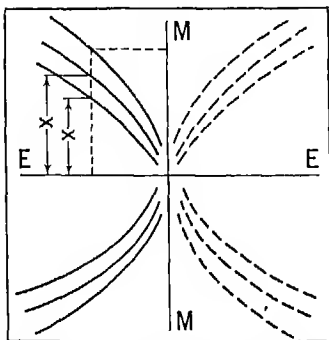


Figure 143 Parabolas Produced by O_2^+ Particles (Lowest), O^+ Particles (Middle), and a Lighter Particle, Such as N^+ (Top)

The extent of the deflection of a particle depends upon the strengths of the deflecting fields, the mass, charge, and velocity of the particle, and the dimensions of the apparatus. When acted upon by both fields simultaneously, particles possessing the same mass and the same charge (or the same e/m) will strike the screen or plate at different points, depending upon their velocities, along a curve that lies between $E-E$ and $M-M$. Particles possessing different masses or charges produce other curves, each curve representing the points at which all particles having the same ratio of e/m strike the screen. From comparisons of the curves made by different kinds of particles, some of which have known masses and charges, all the particles can be identified and their masses determined. The curves lie to the right or left of $M-M$ and above or below $E-E$ depending upon the directions of the deflecting fields.

3 Discovery of the Isotopes of the Stable Elements

During the course of many experiments with positive particles, Thomson was puzzled by the appearance of two parabolas when-

ever neon was present in the tube. Both of these curves appeared to be due to atoms of this element, although neither corresponded exactly to the accepted atomic weight of neon, 20.2. The possibility that they might be due to other particles had to be eliminated, and this was done. The two parabolas showed that they were produced by particles which possess masses of 20 and 22, respectively, as compared to 16 for the atom of oxygen. This could mean but one thing. There must be two kinds of neon atoms (three are now known), and the atomic weight of 20.2, which is usually accepted as the atomic weight of the element, is the average of these two values. The two kinds of neon are, however, always mixed in the same proportion, since the average atomic weight does not vary.

4 Aston's Mass Spectrograph

Thomson's classical experiments with positive rays led directly to the discovery of the isotopes of the stable (non-radioactive) elements. Thomson's original apparatus was considerably modified by Aston, who used it to determine the number of isotopes of all the elements and their atomic weights. In Aston's apparatus (Figure 144) the electrical and magnetic fields are applied at right

angles to each other and at different positions, as shown in the figure. The particles are first deflected by the electrical field, and the original beam is thus divided into a number of parts because of the different degrees of deflections of particles of different velocities. The deflected particles then pass into the magnetic field where they are again deflected. If the positions of the different parts of the apparatus are properly adjusted, the magnetic field will bring to a focus on the photographic plate all the particles which have the same charge and mass but different velocities. Instead of being scattered along a parabola as in Thomson's tube, the particles are all concentrated on a very small area of the plate. Thus, a few which would produce a very faint parabola may be recognized much more clearly by Aston's method. By measuring the position of the spot which is produced by any one kind of particles, in relation to the spots formed by other particles of *known* charge and mass, the ratio of the charge to the mass (e/m) for that kind of particle is determined. Later modifications of Aston's apparatus are said to give results which are accurate to one part in ten thousand. Because it separates particles of different masses into a spectrum, somewhat like the spectrum into which a

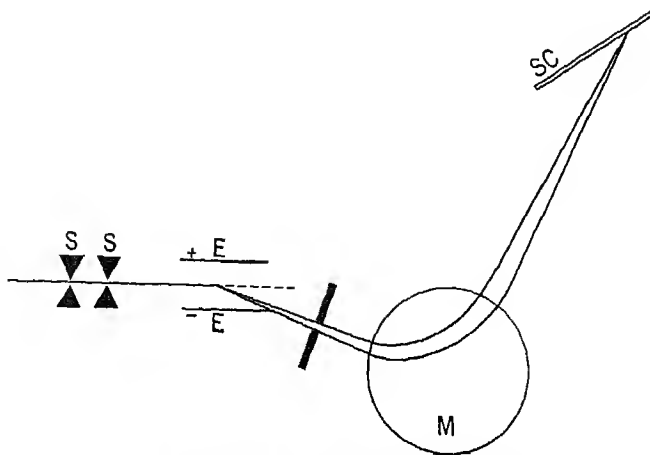


Figure 144. Aston's Mass Spectrograph

SS is the slit system; EE, the electrical field; M, the magnetic field; and SC is the screen or photographic plate.

TABLE 12
Isotopes of Some of the Elements *

Element	Mass Numbers of Isotopes (in order of abundance)
Hydrogen	1, 2, 3
Helium	4, 3
Lithium	7, 6
Beryllium	9
Boron	11, 10
Carbon	12, 13
Nitrogen	14, 15
Oxygen	16, 18, 17
Fluorine	19
Neon	20, 22, 21
Sodium	23
Magnesium	24, 25, 26
Aluminum	27
Silicon	28, 29, 30
Phosphorus	31
Sulfur	32, 34, 33
Argon	40, 36, 38
Potassium	39, 41, 40
Calcium	40, 42, 43
Titanium	48, 46, 47, 49
Iron	56, 54, 57, 58
Cobalt	59, 57
Nickel	58, 60, 62, 61, 64
Copper	63, 65
Zinc	64, 66, 68, 67, 70
Arsenic	75
Selenium	80, 78, 76, 82, 77, 74
Bromine	79, 81
Krypton	84, 86, 82, 83, 80, 78
Rubidium	85, 87
Strontium	88, 86, 87, 84
Zirconium	90, 92, 94, 91, 96
Silver	107, 109
Cadmium	114, 112, 110, 111, 113, 116, 106, 108
Tin	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
Antimony	121, 123
Tellurium	130, 128, 126, 125, 124, 122, 123, 120
Iodine	127
Xenon	132, 129, 131, 134, 136, 130, 128, 124, 126
Cesium	133
Barium	138, 137, 136, 135, 130, 132
Gold	197
Platinum	195, 194, 196, 198, 192
Mercury	202, 200, 199, 201, 198, 204, 196
Lead	208, 206, 207, 204

* In most instances radioactive isotopes have not been included

spectrograph analyzes a beam of light, Aston's device has been called the *mass spectrograph*

5 Aston's Determination of Isotopes

The results secured by Aston's original mass spectrograph indicated that the masses of the atoms of all elements are whole numbers when represented on the usual scale of atomic weights. This was true in all cases except hydrogen for which the usually accepted value of 1.008 appeared to be correct. Later results, however, proved that this first conclusion was incorrect. When Aston's apparatus and methods were refined and modified so that the results were accurate to one part in ten thousand, it was found that the mass of an atom of each of the isotopes of some elements was slightly less than a whole number as compared to oxygen. For others, the mass was found to be slightly greater than a whole number.

A list of the isotopes of some of the more common elements is given in Table 12. The different isotopes of an element are identified by their mass numbers, that is, the whole numbers nearest their atomic weights.

6 The Packing Effect

Table 13 lists the masses of atoms of some of the isotopes of the lighter elements. It will be noted that the mass of any atom differs slightly from a whole number. In some cases it is slightly greater and in others slightly less than a whole number. According to the theory of nuclear structure that has already been presented, the nucleus of any atom (except hydrogen) is composed of neutrons and protons. An examination of the values in Table 13, however, shows that the actual mass of the atom does not correspond to the total mass of the protons and neutrons that the atomic nucleus is assumed to contain, although we do not know of any other particles that could act as units of the structure of the nucleus. Therefore, if we still assume that the nucleus contains only protons and neutrons, we must assume

TABLE 13

Masses of Atoms of Isotopes

Element	Mass Number of Isotope	Mass of Atom (by physical methods)
Lithium	6	6.0167
	7	7.0180
Carbon	12	12.0036
	13	13.0076
Nitrogen	14	14.0073
	15	15.0048
Neon	20	19.9986
	22	21.9985
Magnesium	24	23.9938
Chlorine	35	34.9796
	37	36.9777

that these particles suffer a slight reduction of mass when they are packed together to form the nucleus of an atom. This loss of mass is called the *packing effect*. As we shall show in the following sections of this chapter, there is proof that the mass that is lost is converted into energy.

If the packing effect upon the masses of protons and neutrons is real, one would expect the effect to vary somewhat in different atoms. An examination of the masses of atoms, as shown in Table 13, shows that the effect does vary. The effect is about the same for the isotopes of one element, but when we compare the losses of mass for the isotopes of one element with the losses for the isotopes of another element, we find marked differences. In the atoms of chlorine, for example, the loss of mass by protons and neutrons appears to be greater than the loss in atoms of lithium.

7. The Equivalence of Mass and Energy

About 1905, Einstein suggested that mass and energy are equivalent and that the quantity of energy E equivalent to the mass m could be calculated by the equation

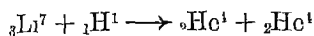
$$E = mc^2,$$

where c is the velocity of light. This principle suggested many interesting possibilities. For example, the nucleus of an atom must be a stable system, otherwise it would not exist. Since it is stable, energy must be expended in separating the different particles that compose it. Now if mass and energy are really equivalent, the expenditure of energy in breaking up the nucleus of an atom should result in an increase in mass, and hence the combined weight of the free protons and neutrons produced by the disintegration of a nucleus should be greater than that of the nucleus itself. The consideration of the helium atom, or rather the alpha particle, indicated that this was true. This particle contains two protons, each having a mass of 1.00758, and two neutrons, each of 1.00893.¹ The four particles should have a combined mass of $(2 \times 1.00758) + (2 \times 1.00893)$, or 4.03302 mass units. But as the mass of the alpha particle is actually only 4.00280 mass units, it appears that $4.03302 - 4.00280$, or 0.03022, units of mass disappeared when the four particles combined to make the nucleus of an atom of helium. By Einstein's equation this quantity of mass should be equivalent to 1.5×10^{-6} ergs of energy per alpha particle. For one gram-molecular weight of helium, the quantity of energy involved would be 2.7×10^{10} ergs, which is equivalent to 190,000 kilowatt hours. The same quantity of energy would be required to break up the nuclei in a gram-molecular weight of helium, and this change would be attended, according to the theory, by a corresponding increase in mass as represented by the masses of the separated protons and neutrons.

In 1932, experimental proof of Einstein's theory concerning the equivalence of mass and energy was obtained. Lithium was bombarded with high-speed protons. It was found that alpha particles were ejected from

¹ The unit of mass used here is one sixteenth of the mass of the oxygen isotope that has an atomic weight of 16. It is equal to 1.6603×10^{-24} gram.

the atoms of lithium as a result of the bombardment¹



The masses of all the particles involved in this reaction are known from measurements made by means of the mass spectriograph (page 276). The particles on the left have a combined mass of 8.0241, while the two alpha particles (on the right hand side) have a combined mass of 8.0056. It seems certain, therefore, that in this reaction there is a loss of 0.0185 unit of mass, which by Einstein's equation should be equivalent to 27.2×10^{-6} ergs of energy. Actually, the two alpha particles were found to possess 27.6×10^{-6} ergs, and their energy could have been acquired only by some process associated with the reaction of the lithium nucleus and the proton. Since the theoretical quantity of energy calculated from the loss of mass by Einstein's equation and the actual quantity of energy released during the reaction checked very satisfactorily, the results were considered as almost positive proof that mass and energy are equivalent.

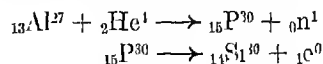
The quantities of energy released in reactions of the kind we have discussed above are enormous as compared to other known reactions which involve similar quantities of materials. For this reason, physicists during the years just preceding World War II became more and more interested in the possibility of obtaining energy by means of reactions involving the combination of protons and neutrons to form atomic nuclei or by converting one kind of nucleus into another.

8 Artificial or Induced Radioactivity

In 1934, aluminum was made to act in a radioactive manner by bombarding it with alpha particles. After the bombardment had stopped, radioactive disintegration contin-

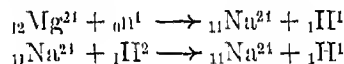
¹ In this and similar equations, the subscripts used represent the atomic numbers and the superscripts the mass numbers of the elements. The mass number is equal to the combined number of protons and neutrons in the nucleus of an atom of the element.

ued for some time and indicated a half-life time for the radioactive element of three to four minutes. Tests indicated that phosphorus, produced by the fusion of aluminum nuclei and alpha particles, was the radioactive element. Its atoms disintegrate to produce silicon and positrons (${}_{-1}e^0$)

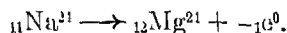


In these equations ${}_0n^1$ represents a neutron, which has a mass number of 1 and no atomic number. The positron, ${}_{+1}e^0$, has no atomic number, but a subscript of 1 is used to account for the fact that the loss of a positron results in a reduction of 1 in the atomic number of the element (${}_{14}\text{Si}^{30}$) which is produced by the disintegration of an atom of ${}_{15}\text{P}^{30}$.

A radioactive isotope of sodium is produced by bombarding magnesium with neutrons or sodium with deuterons (nuclei of deuterium)



The radioactive isotope of sodium that is made by either of these reactions has a half-life period of about 15 hours. It disintegrates to produce ordinary magnesium and electrons:



Element 43, formerly called manganum, has been produced by bombarding molybdenum with neutrons or deuterons. The new name *technetium* has been suggested for this element. Element 85, formerly called alabamine, has been produced by the bombardment of bismuth with alpha particles. It is a radioactive member of the halogen family. The name *astatine* has recently been suggested for it. There seems to be strong evidence that isotopes of this element may occur naturally among the disintegration products of the uranium, thorium, and actinium series of radioactive elements.

Radioactive isotopes of almost all the

elements have now been produced by methods similar to those described above. Some of these disintegrate to produce stable nuclei by emitting positrons, some emit electrons; and a few emit alpha particles

9 The Cyclotron

This is a device by which protons and deuterons of high velocity are obtained for use in bombardments of atomic nuclei. It consists (Figure 145) of a circular brass box, built in two sections, which are connected by means of an insulating material. The two sections are charged, one positively and the other negatively, and the box is placed in a powerful magnetic field. Protons or deuterons are introduced into the center of the box, where they move in a circular path, under the influence of the magnetic field, as all similarly charged particles do. A positively charged particle is attracted by the charge on the negatively charged section of the box (A, Figure 145), and it is repelled by the other section (B). As the particle reaches the gap (G_1) between the two sections, the charges are reversed, i.e., A becomes the positive and B the negative section. This reversal of charge produces an acceleration in the velocity of the particle and, as a result, the circular path in which the particle moves increases in radius. Since the charge is reversed each time the particle crosses the gaps, G_1 and G_2 , the path becomes a spiral of ever-increasing radius. Finally, it leaves the circular box at D with its maximum velocity, which may be as great as 25,000 miles per second, depending upon the strength of the magnetic field. Magnets weighing 80 to 100 tons are used, and even

larger ones are planned. The more powerful the magnet, the more times the particle can be made to cross the gap, and the greater its velocity may become. The high-speed particles thus obtained are then used to bombard materials containing different elements for the purpose of producing transmutations.

10 Tracer Elements

An interesting development of recent years has to do with "tracer" chemistry. The artificially radioactive isotopes of some of the elements have been especially useful in this work. If, for example, we wish to trace the course followed by atoms of phosphorus through a series of reactions involving several precipitations, crystallizations, and other processes, we may prepare as the starting material a compound containing some ordinary, stable atoms of phosphorus and some atoms of its radioactive isotope. As the two kinds of atoms have identical properties, they will remain mixed in a definite proportion throughout any series of changes in which phosphorus may be involved. Because of the radioactivity of some of the atoms of phosphorus, the presence of this element can be detected very easily by means of any of the devices, such as the electroscope, that are used to detect the rays produced by radioactive substances. We may be certain that any precipitate or batch of crystals that exhibits radioactivity contains at least a part of the phosphorus present in the original material. Tracer elements have been especially helpful in the study of many biological processes. By using the radioactive isotope of phosphorus mixed with ordinary phosphorus in the form of a phosphate that is incorporated with food material, it is possible to determine not only the time required for that element to become a part of the phosphate structure of the bones of the body, but also the time that elapses before phosphorus in food passes through the different phases of metabolism and is eliminated from the body. Similarly, we may study the circulation of

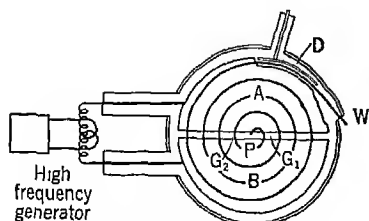


Figure 145 The Cyclotron

the blood by injecting into the blood stream a solution of sodium chloride, if some of the sodium atoms are of the radioactive isotope of that element (page 279). Deuterium and the heavy isotope of carbon and nitrogen (${}^6\text{C}^{13}$ and ${}^7\text{N}^{15}$) have all been used as "tracer" elements in biological research.

11. Nuclear Fission

Natural uranium consists of the three isotopes, which, in accordance with the system explained in the footnote on page 279, we shall represent as ${}_{92}\text{U}^{234}$, ${}_{92}\text{U}^{235}$, and ${}_{92}\text{U}^{238}$. The quantity of the U-238 isotope in metallic uranium is 140 times greater than that of the U-235 isotope and about 16,550 times greater than the quantity of U-234. The three isotopes have almost identical chemical properties, but they differ considerably in the effects resulting from the absorption of neutrons by their nuclei. We shall be concerned at this time with the effect of neutron absorption upon the nuclei of U-235 and U-238.

When a neutron is absorbed by a nucleus of U-235, that nucleus is split into two smaller nuclei of about the same size and from one to three neutrons. All of the liberated particles possess relatively large quantities of kinetic energy. A change of this kind in which an atomic nucleus is split into two fragments of about the same size is called *nuclear fission*. The nuclear fragments are nuclei of radioactive isotopes of elements having atomic numbers from 34 to 57. Figure 146 shows the fission of a ura-

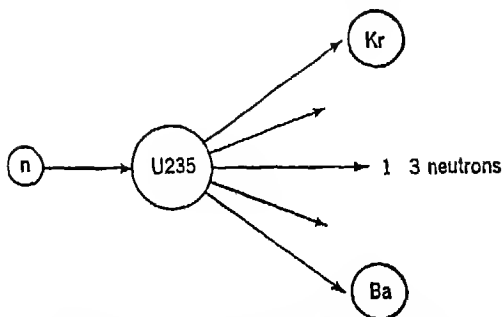


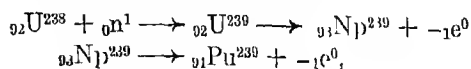
Figure 146. Fission of an Atom of U-235

num nucleus to form the nuclei of barium and krypton.

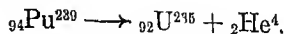
The neutrons ejected during the fission of a single U-235 nucleus may (1) escape into the surroundings, (2) be absorbed by the nuclei of other U-235 atoms, or (3) be absorbed by U-238 nuclei or by impurities in the sample of metallic uranium.

The neutrons that are absorbed by U-235 nuclei may cause the fission of those nuclei. The fission of each nucleus liberates from one to three additional neutrons which may be absorbed by other U-235 nuclei, thus causing the process to be repeated again and again. A self-propagating reaction of this kind is called a *chain reaction*. If more neutrons are absorbed by U-235 nuclei than are lost to the surroundings or absorbed by U-238 and impurities, the fission of U-235 nuclei will continue at an increasing rate, and fission will spread throughout the whole mass of the sample of metal. The energy released is in the form of kinetic energy of the particles produced, and hence is actually heat energy. It is therefore quite likely that, unless the reaction is controlled in some way, the heat liberated will quickly become sufficient to vaporize the entire sample of uranium and even surrounding objects.

Some of the neutrons that are captured, or absorbed, by U-238 nuclei convert that element into neptunium and finally into plutonium by a series of changes which is summarized in the equations



in which ${}_{-1}\text{e}^0$ is used to designate an ordinary electron. ${}_{92}\text{U}^{239}$, an isotope of uranium, ${}_{93}\text{Np}^{239}$, and ${}_{94}\text{Pu}^{239}$ are all radioactive. The first two decay rapidly but ${}_{94}\text{Pu}^{239}$ disintegrates very slowly as follows



The rate of disintegration of plutonium, ${}_{94}\text{Pu}^{239}$, is so slow that we may consider it, for all practical purposes, as a stable element. When plutonium nuclei absorb

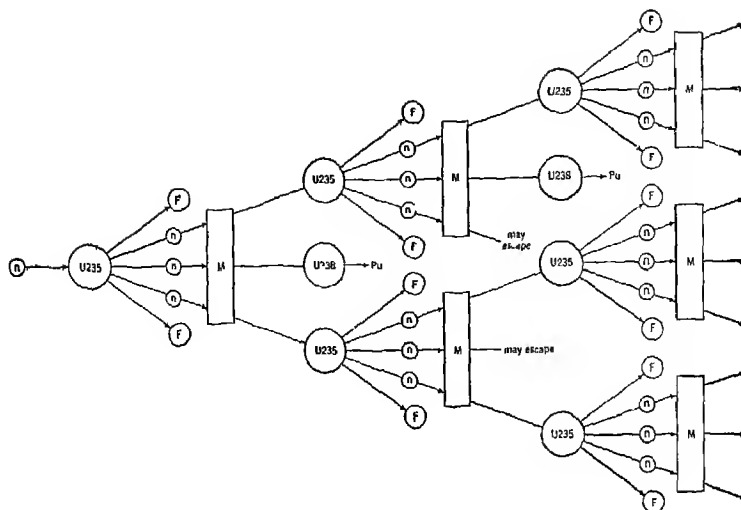


Figure 147 Chain Fission Reaction

M, moderator (graphite) to slow neutrons, n, neutrons, F, fragments of fission of U-235, atoms of elements in middle portion of periodic table, Pu, plutonium

neutrons they may undergo fission in the same manner as U-235 nuclei

The neutrons liberated by the fission of U-235 have such high velocities that they are not very effective in causing the fission of other U-235 nuclei or in converting U-238 into neptunium and plutonium. It is highly desirable that they be slowed down to a velocity that will make their absorption by U-235 nuclei most likely to result in fission, if the chain reaction is to be continued. To accomplish this purpose the reaction may be carried out in a graphite-uranium pile instead of pure uranium metal. Graphite causes neutrons that pass through it to be slowed in velocity, but it does not absorb them to a significant extent. A pile is a structure consisting of blocks of graphite and rods of metallic uranium, which are inserted in openings between some of the blocks. After the neutrons have been slowed by the graphite moderator there is a higher probability that, when they again pass into the uranium, they will cause the fission of any U-235 nuclei that may absorb them (Figure 147).

Unless it is controlled, the reaction may become very rapid, and the temperature may

reach a point at which the entire pile may be vaporized. To prevent this from happening, rods of cadmium or of some other material may be inserted in openings in the pile provided for this purpose. Cadmium absorbs neutrons and therefore reduces the number that can be absorbed and produce fission of U-235 nuclei.

A graphite-uranium pile liberates large quantities of heat. The products of the fission of U-235 nuclei have a combined mass that is about 0.1 per cent less than the mass of the original atoms. For one pound of U-235, the loss of mass during fission has been estimated as equivalent to a sufficient quantity of energy to supply all the power required by a city of 25,000 persons for an entire year. Sometime in the future, this energy will probably become available for industrial purposes.

If and when nuclear fission becomes a practical source of industrial energy, piles such as those we have described will be used. To produce atomic bombs for military purposes, pure U-235 or plutonium must be used. In ordinary metallic uranium there are too many U-238 atoms which absorb most of the neutrons, thus interfering with

the fission of U-235 nuclei. The separation of U-235 from U-238 is very difficult. The two isotopes have almost identical chemical properties, hence chemical methods of separation cannot be used. One method that has been used very extensively depends upon the difference in the rates of diffusion through a barrier of uranium hexafluoride molecules containing atoms of U-235 and U-238. Since the U-235 atoms are lighter, the molecules containing them diffuse more rapidly through the barrier than molecules containing the heavier atoms of U-238. The first portion of uranium hexafluoride to diffuse through the barrier is richer, therefore, in U-235 than the original material. This portion is allowed to diffuse again, and the process is repeated many times in order to get complete separation.

To produce an explosion, two portions of U-235 must be brought very quickly together, and the combined mass of the two portions must be such that the production of neutrons by fission will exceed the number lost by escape.

Plutonium for use in bombs is produced by the absorption of neutrons by U-238 nuclei in an uranium-graphite pile. Since plutonium is a different element from uranium, and consequently has quite different chemical properties, the two elements can be separated by chemical methods.

The discovery of a fissionable isotope of neptunium, ${}_{93}\text{Np}^{237}$, has recently been announced.

12 The Transuranium Elements

Neptunium and plutonium (page 281) are frequently referred to as transuranium elements because they have atomic numbers greater than 92 and therefore lie beyond uranium in the periodic table. The atomic number of neptunium is 93 and that of plutonium is 94. The chemical properties, including the different oxidation states of each element, have been determined. Many of the compounds of plutonium were prepared and studied in the work involved in

the separation of plutonium from uranium during the development of the atomic bomb project. Several compounds of neptunium have also been made.

Elements 95 and 96, or at least isotopes of these elements, have been produced by the bombardment of U-238 and Pu-239 with high-speed helium ions. Element 95 is called *americium*, ${}_{95}\text{Am}^{241}$. It is radioactive, emits alpha particles and has a half-life period of about 500 years. Pure americium hydroxide has been prepared and some of the chemical properties of the element have been studied. Element 96 is called *curium*, ${}_{96}\text{Cm}^{240}$ and ${}_{96}\text{Cm}^{242}$. The two isotopes of this element are radioactive. Both emit alpha particles and have half-life periods of one month and five months, respectively. A new isotope of plutonium, ${}_{94}\text{Pu}^{241}$, has recently been produced by bombarding U-238 with alpha particles. This isotope emits electrons and forms an isotope of americium during radioactive decay.

Studies of the properties of the transuranium elements indicate that they are the first members of a group of elements in the seventh period that corresponds to the rare-earth group beginning with lanthanum and including elements 57-71 in the sixth period. The seventh-period group begins with actinium, No. 89, and includes thorium, protoactinium, uranium, neptunium, plutonium, americium, and curium.

Review Exercises

- 1 Describe the mass spectrophotometer. For what purpose is it used?
- 2 Describe Thomson's experiments which resulted in the discovery of isotopes of the non-radioactive elements.
- 3 How are isotopes different and how are they similar? Why are they classified as varieties of the same element?
- 4 What is meant by the 'packing effect'? What evidence indicates that this effect is real?
- 5 What conclusion is drawn from the fact that the atomic weights of all the elements are

- approximately whole numbers, when we consider the isotopes of different elements?
6. The atomic weights of the isotopes of an element whose atomic number is 38 are 88, 87, and 86. What is the composition of the nucleus of each of the isotopes?
 7. Three isotopes of oxygen are now known. The relative masses of the three kinds of atoms are 16, 17, and 18. Are the chemical methods of determining atomic weights based upon the isotope of mass number 16 or upon a mixture of all three? Would there be any considerable difference between the values of atomic weights based upon the isotope of mass 16 and those based upon the mean atomic weights of the three isotopes? Explain.
 8. Three isotopes of hydrogen are now known. The mass numbers of the isotopes are 3, 2, and 1. How do the structures of the atoms of these three kinds of hydrogen differ?
 9. If the atomic weight of neon, as usually measured, is 20.18, and if its two isotopes have masses of 20 and 22, what is the ratio of the two kinds of atoms in a sample of neon?
 10. What evidence indicates the equivalency of matter and energy?
 11. What changes occur in the formation of artificially radioactive elements? What changes occur when elements undergo fission?
 12. What are the transuranium elements? Why are they so called?
 13. What is a chain reaction? Explain the use of this term in connection with the fission of U-235.
 14. How can the speed of the fission of U-235 be controlled?
 15. How are the artificially radioactive isotopes used as tracers?
 16. Explain the significance of the subscript and the superscript in the expression ${}_{92}\text{U}^{235}$.
 17. Explain the meaning of the following equation

$${}_{7}^{14}\text{N} + {}_{2}^{4}\text{He} \longrightarrow {}_{8}^{17}\text{O} + {}_{1}^{1}\text{H}$$
 18. Since there are three isotopes of oxygen, how many different kinds of molecules of oxygen are present in the air?
 19. Suggest possible methods of separating the isotopes of chlorine.

References for Further Reading

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CARBON

Coal is a portable climate

EMERSON

1. Occurrence

Carbon occurs in nature in the free state and in many compounds. Although it constitutes only about 0.03 per cent of the earth's crust, the vast importance of this relatively small amount of the element is indicated by the 400,000 or more carbon compounds which exist naturally or which have been prepared. This is approximately ten times the number of compounds of all the other elements put together. The human body, like every other organism, is made up of carbon compounds. Carbon or carbon compounds furnish us with practically all of our food, fuel, and clothing. In addition, this element provides most of the energy for our industrial activities, and it is also used in many industrial processes, such as the reduction of metals from their ores. With oxygen and hydrogen it ranks as one of the three or four elements most important to the existence of man.

Carbon dioxide is the most familiar of the gaseous compounds of carbon. It is produced by oxidation in the body and is removed through the lungs. Exhaled air contains more than 140 times as much carbon dioxide as inhaled air. Large quantities of it are also thrown into the atmosphere by household or industrial furnaces in which wood, coal, coke, oil, or gas is burned. To offset the additions to the atmosphere from these sources, plants remove carbon dioxide from the air, using it as one of the raw materials from which they manufacture starches, sugars, and related substances. Petroleum

is composed almost entirely of compounds of carbon and hydrogen. These compounds are called hydrocarbons. The many products of the petroleum refining industry — gasoline, kerosene, fuel oil, motor oil, petrolatum, paraffin — are mixtures of hydrocarbons. Natural gas, also, consists of hydrocarbons, particularly methane, CH_4 . The carbonates are often important sources of some of the metals, and two of them, calcium and magnesium carbonate, form vast deposits of sedimentary rocks, called limestones and dolomites. Calcium carbonate is also the principal constituent of chalk, coral, and the shells and skeletons of many aquatic forms of life.

Free carbon is found in several forms. Coal contains the free element, also hydrocarbons, and other more complex carbon compounds, owing their origin to the plants from which the coal was formed. Anthracite coal contains a much larger percentage of free carbon than bituminous. Coke which is made by the distillation of coal, and charcoal which is made by the distillation of wood, are practically pure forms of carbon, except for the mineral matter that forms ash when they are burned. Lampblack and soot are also composed of carbon. Smoke is black when it contains particles of carbon and other dark-colored materials that have escaped complete combustion.

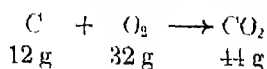
Free carbon occurs in three forms. One of these is the form of the materials mentioned in the preceding paragraph — coke, charcoal, lampblack; these are usually

classified as *amorphous* (non-crystalline) carbon, although at least some of them are composed of very small crystals. *Diamond* and *graphite*, two allotropic forms of free carbon, are both crystalline.

DIAMOND

2 History and Occurrence

In 1816, Davy proved that diamond is a form of pure carbon by converting it into carbon dioxide. He found that the weight of carbon dioxide produced by the oxidation of diamond corresponded to the weight of the entire quantity of diamond consumed.



Lennaut had previously found that the diamond contains carbon and that it burns in pure oxygen to produce carbon dioxide.

The earliest diamonds of which we have any record were found in India. In the early part of the eighteenth century mines were opened in Brazil. However, both these sources were overshadowed in importance when, in 1867, diamonds were found in South Africa. The first of the African diamonds was discovered quite by accident on the banks of the Orange River, where it had probably been deposited in the mud left by the flooded stream. A few years later the famous mines near Kimberley were opened. Here diamonds occur in very deep vertical "pipes," which are probably the necks of old volcanoes. The diamonds are embedded in a rocky mass of material which fills the "pipes" and which is called "blue ground." Free carbon was probably liberated by the reduction of its compounds when the material composing "blue ground" was still hot. Subsequent cooling under high pressures resulted in the crystallization of the element in the form of diamond. Shafts with branching tunnels and galleries are sunk into the material filling a pipe. The "blue ground" removed from this shaft is crushed, and the diamonds are separated by

shaking. Water is added to remove the lighter portions of earth. This gives a "concentrate" in which the diamonds are collected. From this the diamonds are completely separated by carrying off the worthless materials in a stream of water which, mixed with the concentrate, flows over plates covered with grease. Diamonds are caught and held by the grease, which has more attraction for them than water has.

The world's largest diamond mine, the Premier, was opened in the Transvaal in 1903. This is an extremely large pipe. Here was found, in 1905, the largest diamond yet discovered. This uncut stone was called the Cullinan diamond. It weighed 3026 carats, or a little more than one and one-third pounds. It was presented to the King of England and was later cut into a number of gems. Two of them, weighing about 516 and 310 carats, are among the largest cut stones in the world.

The value of a diamond depends upon its weight and freedom from flaws and impurities. Its weight is expressed in carats. A carat is about 0.2 g. Although uniformity of color is of great importance, coloring may enhance rather than decrease the value. The Florentine diamond is yellow, and the Hope diamond is blue. Small diamonds, inferior in value and badly colored, can be produced artificially. Moissan was the first to produce them. In 1893, he dissolved carbon in melted iron and poured the liquid into water. A crust of solid formed, enclosing a mass of still liquid material. As the interior cooled, enormous pressure developed due to the expansion of iron, containing dissolved carbon, upon solidification. As the iron crystallized, some of the carbon separated and thus formed tiny diamonds under the influence of the high pressure inside the mass of iron. The iron was removed, finally, by the addition of hydrochloric acid, in which diamond does not dissolve although iron does. This method of producing diamonds has not proved practical, and hence is in no way a competitor of the "natural" diamond industry. "Paste" diamonds are mere imitations, made of glass and cut in the same designs as diamonds.

The density of diamond is 3.5 g per cc. It is very brittle and in hardness ranks above all other natural substances. Some of the car-

bides (binary carbon compounds) are also extremely hard. Even the diamond may be scratched by the carbide of boron, and tungsten carbide has been used in the place of discolored diamonds in the teeth of stone-saws. The carbide of silicon (SiC), is also very hard and is used for grinding and polishing. Diamond is inactive and resists the action of most substances which attack vigorously other forms of the element and also its compounds. It begins to burn in air, however, at about 900° and in pure oxygen at about 700° .

Rough diamonds are usually not very lustrous. The cutting of a rough stone consists in producing facets which are so arranged that light entering the crystal will be reflected back and forth from one facet to another. Because of its high index of refraction and great dispersing power, diamond breaks up white light into different colors. Cutting must also bring out this property of the stone.

Black diamonds, many of which are obtained in Brazil, are called *carbonadoes*. These and other badly colored stones are set in the teeth of saws, or in the bits of drills, which are used to cut through stone. They are also used in grinding and polishing hard materials. Diamond dust is used to polish diamonds and other precious stones.

GRAPHITE

3. Occurrence and Production

The second crystalline allotropic form of carbon is now called graphite. It was once thought to be some compound of lead and was called *plumbago*. Native graphite is found in many parts of the world. The most important deposits are those of Ceylon, Siberia, Madagascar, and Korea. Some is

also found in Austria, Germany, Mexico, Canada, Italy, and the United States (New York).

Any form of carbon vaporizes when heated to a temperature of about 3500° in the absence of air; upon cooling, the vapor condenses to form crystals of graphite. The commercial production of graphite is based upon this principle. The Acheson process is used at Niagara Falls to make graphite on a large scale from coal. An electric furnace (Figure 148) is employed to heat a charge consisting of coke and lumps of hard coal. A small central core of finely granulated carbon connects the electrodes and acts as a conductor of the current, since the coarse lumps of coal conduct very poorly. The charge is covered with a layer composed of sand and carbon to exclude the air. An alternating current supplied by a generator passes through the charge and, because of the resistance, liberates enormous quantities of heat, which causes the conversion of the carbon in the coal into graphite. Ferric oxide acts as a catalyst in the transformation. Coal usually contains a sufficient quantity of this substance to render the change sufficiently rapid.

4 Properties and Uses

The density of graphite is 2.2 g per cc. It is very soft, so soft that it leaves marks when rubbed across a sheet of paper. The name graphite, from the Greek word which means "to write," was given to the substance because of this property. It conducts the current of electricity better than any other form of carbon. Like diamond it is chemically inert, resisting the attack of most reagents. It burns in oxygen at a temperature around 700° .

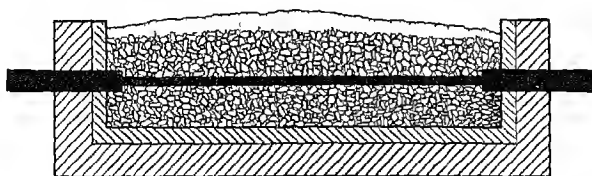


Figure 148 The Production of Graphite in the Electric Furnace

Because of its chemical inactivity graphite is used to make crucibles in which metals are melted in the manufacture of alloys and high-grade steel. A mixture of graphite and clay is used to make the crucible, the clay acting as a binding agent for the crystals of graphite and rendering them somewhat more resistant to oxidation at high temperatures. It is also widely used in the manufacture of electrodes, brushes, and other parts of electrical devices. Powdered graphite is used to coat wax molds, which are later used as electrodes for the deposition of metals. This is the method of producing the plates used in the electrotyping process of printing. Graphite is an important lubricant because of the tendency of its small crystalline plates to slide over one another under friction. It is used to lubricate wooden parts of machines and also metal bearings which are exposed to sand and dust or high temperature, which would render a lubricating oil valueless. Suspensions of "deflocculated" graphite in water and in oil are also used as lubricants. These are called "aqua-dag" (deflocculated Acheson graphite) and "oil-dag," respectively. Graphite is also used as a pigment in paints, and in stove polish, and as a lining for foundry furnaces. The "lead" of a pencil is composed of a mixture of graphite, clay, and wax. Sometimes, lampblack, silica, and other substances are added to produce pencils of special grades. The "hardness" of the "lead" depends upon the proportions in which the constituents are mixed. Soft "leads" contain more graphite or lampblack and less clay or silica than hard "leads."

5. The Crystal Structures of Diamond and Graphite

Many of the properties of diamond and graphite depend upon their respective crystalline structures. The crystal lattices of the two allotropes are shown in Figures 149 and 150. The diamond crystal belongs to the cubic system (page 237). Each carbon atom is surrounded by four other atoms which are located at the corners of a tetrahedron. We may think of each carbon atom as

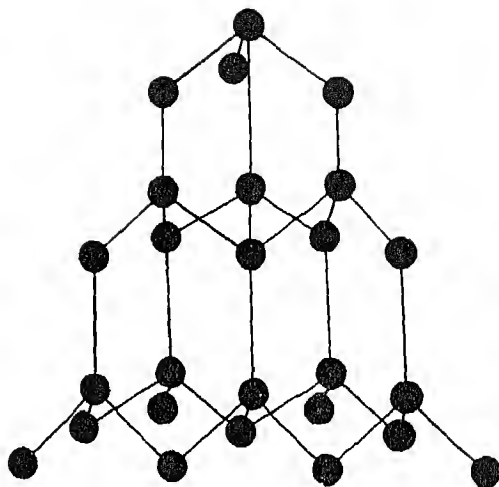


Figure 149 The Structure of a Crystal of Diamond

joined to four others and exhibiting, therefore, a valence of four in the crystal just as the element does in its compounds. The extreme hardness of diamond indicates that the valence forces in the crystal are especially strong. In the crystal of graphite, carbon atoms are arranged in hexagonal rings of six atoms each, all of which lie approximately in the same plane. The crystal may break up into relatively thin plates because the forces that tie one plane to another are relatively weak. For the same reason the different layers easily slide over one another. The use of graphite as a lubricant depends upon this feature of its crystalline structure.

In both diamond and graphite the bonds between carbon atoms are of the covalent, or atomic, kind. Both are therefore rather poor conductors.

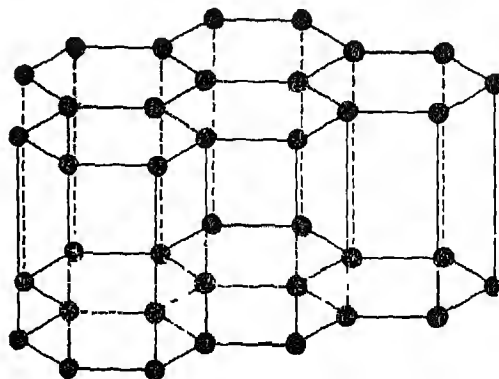


Figure 150 The Structure of a Crystal of Graphite

of the electrical current, although graphite is considerably better than diamond. Diamond is a very poor conductor because the valences of the carbon atom are completely satisfied and all electrons are used in uniting the atoms. In graphite, however, the structure indicates that only three of the possible four valences are employed. Some of the electrons are thus unused and are free to move under the influence of an electrical potential.

The allotropic modifications of carbon are characterized by different energy contents. We should expect such differences upon the basis of the differences in the spacing of carbon atoms and the strengths and number of the valence bonds in the crystals of diamond and graphite. The burning of 12 g. of diamond to form carbon dioxide liberates 94,300 calories, the burning of the same weight of graphite liberates 94,800 calories.

OTHER FORMS OF CARBON

Many forms of carbon are said to be amorphous, although X-ray analysis shows that they are composed of crystals of the same structure as those of graphite. These forms, such as charcoal, usually show more porous structures than graphite or form soft and very bulky powders. The most important forms of amorphous carbon are coal, coke, charcoal, lampblack, gas carbon, and bone-black.

6. Coal

The industry of the world depends largely upon coal for its supply of energy. This energy is released by burning the coal beneath boilers in which steam is generated. The energy of expanding steam is then converted into electricity or into mechanical forms of energy, such as the revolution of wheels. Not all the energy which industry uses comes from coal, but this source, at present, is by far the most important. Fuel oils and gases are often used in place of coal to generate steam in boilers and in Diesel engines, in internal combustion engines, and even in household furnaces. Water power, also, is an important source of energy. Other

sources of energy, such as the heat of the sun, the tides, the winds, and ocean waves, have been suggested, and some of them are utilized to a limited extent. It is now predicted that "atomic energy" will be available for large-scale industrial utilization in the relatively near future.

Because of coal's importance as a fuel, the industrial prosperity of a country depends in large measure upon that country's supply of this mineral. The world produces about one and one-half billion tons of coal each year. The United States produces about 650,000,000 tons annually from the deposits found in Pennsylvania, West Virginia, Indiana, Kentucky, Illinois, and Tennessee.

The origin of coal goes back to an early geological age, when some parts of the earth were covered by more dense vegetation than that with which we are familiar. This vegetable matter collected in deep layers, and, ultimately, was converted into beds of coal. Decay was prevented by geological changes that submerged the deposits beneath the sea and covered them with layers of sediment, thus excluding the air. Chemical changes then slowly converted the deposited vegetable matter, first into what we call *peat*, then into *lignite* or brown coal, then into *bituminous* or soft coal, and, if the process continued long enough and under the proper conditions, finally into *anthracite* or hard coal. This process is called *carbonization*, since the slow changes that occur result in the liberation of the hydrogen, oxygen, and nitrogen originally present in the plants and in an increase in the percentage of carbon. Table 14 shows the relative amounts of these elements, and also the percentages of uncombined water and ash, in wood and in the different forms of coal. Increased pressures and temperatures have undoubtedly influenced carbonization in many deposits of coal. Many of the changes involved in the production of coal from vegetable matter have occurred, of course, after the deposits have been elevated above the sea by geo-

TABLE 14

Analyses of Different Kinds of Coal*

(Percentages)

Sample	Water	Volatile matter	Fixed carbon	Ash	Dried Sample				Heating value (B T U per lb.)
					Carbon	Hydrogen	Nitrogen	Oxygen	
Wood	7.4			0.4	50.0	6.0	0.1	43.0	4,500
Peat (air dried)	10.0	50.0	25.0	10.0	59.0	5.0	2.9	32.0	4,300
Lignite	33.0	29.0	29.0	7.0	42.5	7.0	0.8	42.0	6,500
Bituminous coal	3.4	35.5	51.3	9.7	71.0	5.2	1.4	9.0	13,000
Anthracite coal	3.3	3.27	85.0	9.1	85.5	3.3	1.1	3.5	13,350

* The analyses given in this table are representative values and are not to be considered as indicating the percentages of the various constituents to be found in every sample of fuel in a certain class. The percentages of water and ash are especially likely to vary over wide ranges. The volatile matter refers to the gases that are liberated upon heating dried samples of coal, some carbon is thus removed as volatile compounds containing hydrogen and other elements. Fixed carbon refers to the carbon that is *not* volatilized upon heating, it remains as the free element. 1 B T U = 252 calories.

logical changes which are slowly but gradually, even now, changing the shapes of continents and oceans. Coal, especially the bituminous variety, contains many different compounds, many of which have not been identified definitely.

7. Coke

When coal is heated in the absence of air, the volatile constituents are driven off, leaving behind free carbon and the mineral substances which constitute the ash when coal is burned. The residue is called *coke*. The coal is said to be *destructively distilled*. During the conversion of coal into coke, many of the rather complex compounds found in coal and containing carbon, oxygen, nitrogen, and hydrogen are broken down into simple and more readily volatile substances, which are distilled. The extensive amounts of coke used in the production of water gas (page 111) and in the metallurgy of iron, where it is employed to reduce the oxides of iron to the free metal, make the coke industry one of great importance. Some coke is used as a household fuel, where its high heat value and its combustion without the production of smoke make it very desirable. Its use is restricted, however, because of its price and because it is difficult to ignite. As compared with coal it is not easily ignited,

because it contains none of the volatile substances, which have low kindling temperatures, and which are present in coal, particularly in coal of the bituminous variety.

Coke was formerly produced entirely in beehive ovens (Figure 151). The coal was loosely placed in the oven and heated in a limited supply of air. The combustion of a part of the coal converted the remainder into coke. The volatile substances were allowed to burn at the outlet of the oven. The beehive type of oven has now been largely replaced by ovens designed to permit the recovery of the by-products distilled from the

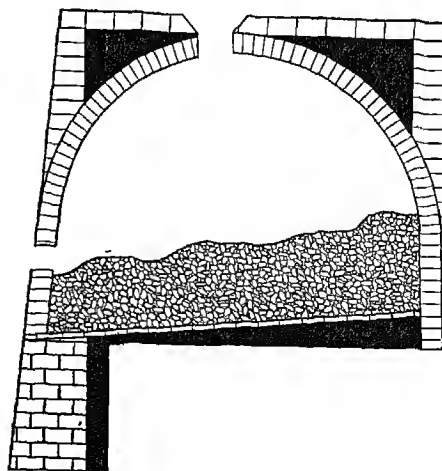


Figure 151 Beehive Coke Oven

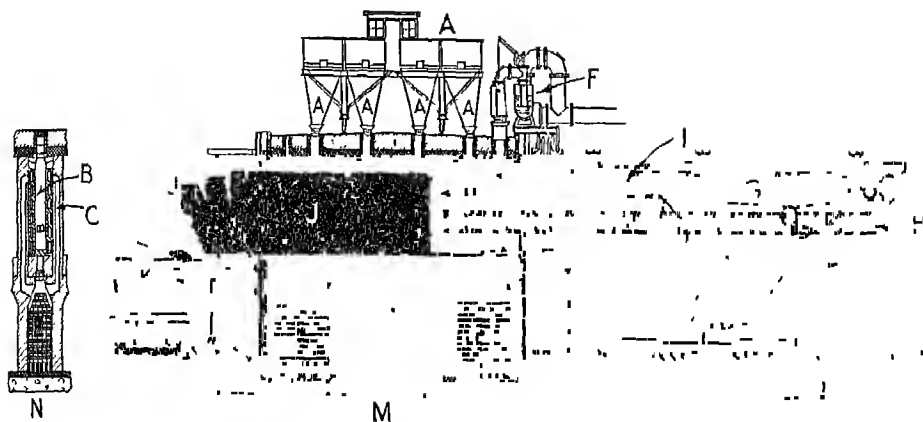
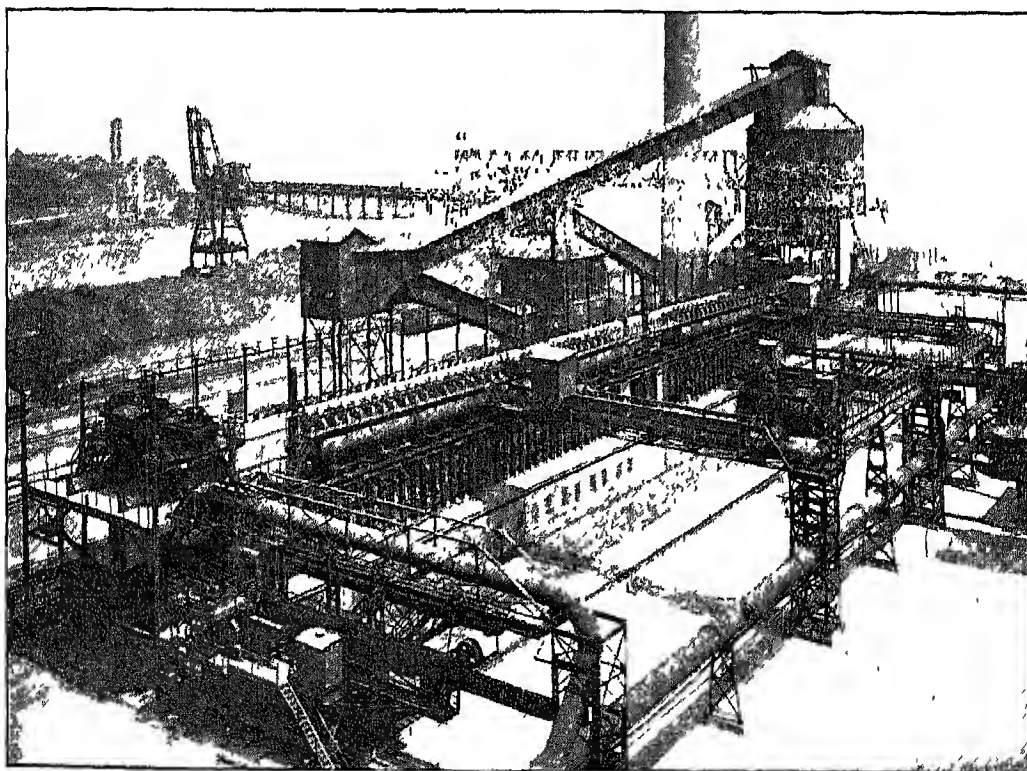


Figure 152 Cross-Section of a By-Product Coke Plant

N, section through retort (B) as seen from one end M, a section taken lengthwise of the retorts. The coal is fed into the retorts through the carriers (A) and is heated by flames and hot gases, produced in C by the burning of coal gas in air that has been heated in E. The gases resulting from the combustion pass out through one compartment E, thereby heating it, while air is entering through the other. The coke (J) is pushed out of the retort by the pusher (H) into cars (K) where it is quenched. The coal gas passes out of the retort through F to the various units of the purifying plant.



Courtesy of Koppers Construction Company

Figure 153 A By-Product Coke Oven Plant

coal These products include ammonia, coal gas (consisting principally of hydrocarbons), benzene, toluene, and coal tar. Many substances used in the manufacture of dyes, drugs, and other chemicals are obtained by further distillation of the tar.

Coke ovens which allow the recovery of the volatile parts of the coal are called "by-product" ovens. A diagram of such an oven is shown in Figure 152. The coal is heated by burning a part of the gas produced in the operation of the plant. Soft, or bituminous, coals give the largest yields of by-products, but anthracite or semi-anthracite gives the best grades of coke. When used in metallurgical operations, coke must be fairly hard and strong to withstand the weight of the charges in the furnaces without crumbling. Coke from bituminous coal is usually too soft, although a good metallurgical grade can be produced if the soft coal is pre-heated before it is placed in the coking ovens.

8 Production of Charcoal

Charcoal is made by heating wood in the absence of air. In the process wood is *destructively distilled*. This means that the hydrogen, oxygen, and some of the carbon and other elements are removed, because some of the materials in the wood decompose into volatile compounds of these elements. In the early history of the industry, piles consisting of short lengths of wood were covered with earth and ignited. A limited supply of air burned some of the wood and converted the remainder into charcoal. As in the beehive coke oven, the volatile materials derived from the wood were burned.

In the modern charcoal plant, iron cars are loaded with hard woods and pushed on a track into a large retort which is heated by fires underneath. The volatile products escape through pipes in the top of the retort into condensers. The liquid which condenses is called *pyroligneous acid*. From it are obtained three very important products: acetic acid, acetone, and methyl (wood) alcohol. The wood distillation in-

dustry has suffered greatly from the development of a method by which methyl alcohol is synthesized from carbon monoxide and hydrogen (page 116).

9. Properties and Uses of Charcoal

Charcoal is used in limited quantities as a fuel. Its greatest use is as a clarifying and decolorizing agent for certain liquids, such as sugar solutions, syrups, acids, extracts, vegetable oils, and petroleum products. This use depends upon the ability of amorphous carbon — particularly charcoal — to *adsorb* certain types of molecules, among which are the molecules of substances responsible for the discoloration of many liquids which are colorless when pure. *Adsorption* is a surface phenomenon in which the molecules are attracted and held by forces existing on the *surfaces* of particles of the adsorbing agent — particles of a solid or a liquid.

Charcoal also adsorbs certain gases; the extent to which it does so depends upon its own physical character, upon the properties of the gases, and upon the temperature and pressure. Adsorption is greatly increased if the surface of the charcoal is extensive, hence finely divided charcoal adsorbs much more gas than larger particles. The total surface of 1 ml. of very finely powdered charcoal may be as great as 1000 square meters. The charcoal made from the shells of coconut has a very high adsorptive capacity. The effect of temperature is shown by the use of finely divided carbon in removing the last traces of air from evacuated containers, the charcoal is placed in a tube connected to the container, and the tube is then cooled by liquid air. The pressure can thus be reduced to about 0.00001 mm. The effect of the properties of the gas is shown by the different extents to which charcoal adsorbs chlorine and oxygen. The more readily condensed gases — those liquefied at relatively high temperatures and small pressures — are adsorbed to a greater extent than others. Chlorine, for example, with a critical temperature of 114°, is adsorbed to a much greater extent at ordinary temperature than oxygen, which has a critical temperature of -118°. It is for this reason that adsorption by charcoal in a gas mask is an effective

tive means of removing chlorine and certain other poisonous gases from air. If the charcoal is cooled, however, to a temperature near the critical temperature of oxygen, that gas is also strongly adsorbed. Charcoal is *activated* to increase its adsorptive capacity by heating it in steam, which breaks down the granules and removes gases already adsorbed.

During World War I it became necessary to devise gas masks to protect troops from poisonous gases. The air to be breathed was passed through canisters filled with materials which removed the poisonous gases but which allowed the air to pass through. Some of the materials used in certain kinds of gas masks removed the poisonous substances by reacting chemically with them. The efficiency of the mask depended usually, however, upon the ability of the charcoal which it contained to adsorb the gases. The best charcoal for this purpose was a hard variety, prepared from coconut shells, peach pits, sugar, or from certain varieties of wood carbonized under pressure. Charcoal-filled gas masks are also used in peacetime to protect workers who may be exposed to poisonous gases. Activated charcoal is used, also, to adsorb the vapors of gasoline which are mixed with the methane of natural gas. The gasoline is recovered by heating the charcoal. Soft, activated charcoal is most efficient in clarifying and decolorizing liquids.

10. Lampblack and Carbon Black

Finely divided carbon is produced by burning natural gas, tar, or oils in a limited supply of air. The best grade is produced from natural gas, and it is this product that is commonly called *carbon black*. The carbon produced from other materials is called *lampblack*. In the presence of a limited supply of oxygen, gas burns with a smoky flame, because of the small particles of carbon that escape combustion. This flame plays upon one side of a revolving drum upon which the soot, or lampblack, is deposited. A knife on the other side scrapes off the deposit as the drum rotates. The product is a very finely divided black powder, which consists principally of free carbon. About 130,000 tons are produced annually in this country. Its principal use is in the compounding of the

mixture used in manufacturing automobile tires. It increases the resistance of the tires to wear, and makes a tougher, stronger, and more resilient fabric. It is also used in the manufacture of many other rubber articles.

Large quantities of carbon black are also used to make printer's ink, typewriter ribbons, India ink, and carbon paper. Because of carbon's inactivity and insolubility, print is not bleached by reagents, such as chlorine, which destroy records made with ordinary ink, and it does not run or smear when it is wet. Carbon black is further used as a paint and enamel pigment, in phonograph records, and shoe, stove, and other polishes.

11. Bone-Black

Bone-black, or animal charcoal, is produced by the destructive distillation of bones and, sometimes, other kinds of organic matter obtained from meat-packing plants. Bones are composed of about 10 per cent of mineral matter, of which calcium phosphate is the principal constituent. Bone-black contains, therefore, only a small percentage — about 10 per cent — of charcoal. The mineral matter may be removed from bone-black by dissolving the calcium phosphate in hydrochloric acid. Usually, however, the bone-black is used as it is prepared. Its chief use is in the sugar refinery. Crude sugar has a yellow or brown color that is removed by dissolving the sugar in water and filtering the colored solution through beds of bone-black. The presence of mineral matter renders the filtering layer more porous and the dispersion of the finely divided carbon through this mass insures an enormous surface of the adsorbing material. The coloring matter of the sugar solution is thus removed and a white crystalline product of a high degree of purity is then prepared by the evaporation of the filtrate.

12. Gas Carbon

Soft coal is distilled in coke ovens to produce illuminating gas and other by-products.

The gas supply of many cities is produced in this manner. Some of the hydrocarbons in the gas are decomposed, or "cracked," by the high temperature of the retorts. As a result, some hydrogen escapes in the gas and carbon is deposited on the walls. This carbon is gray in color, and is harder and more crystalline than other forms. It conducts the current fairly well, and is used, therefore, to make the carbon rods or pencils used in arc lights and the electrodes for electrolytic cells in which either the solutions or the substances liberated would attack electrodes made of metal or other materials.

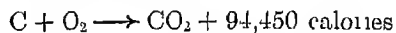
13 Physical Properties of Carbon

In addition to the specific properties possessed by the different forms of carbon, certain other properties are common to all the forms. Carbon is odorless and tasteless. It is insoluble in water and in the ordinary solvents, such as alcohol, ether, benzene, and chloroform. It does dissolve slightly in some melted metals, in which it produces marked changes in properties. One hundred pounds of molten iron will dissolve about one pound of carbon. This solution of carbon in iron is important in the metallurgy of iron and steel. Carbon is always present in the product of the blast furnace, since the ores of iron are reduced by coke. The properties of iron depend in large measure upon the percentage of carbon which it contains, and the same factor is principally responsible for the differences in properties of iron and steel. At about 3500°, carbon passes into the vapor state under ordinary pressures and, upon condensing, forms graphite. When heated to a sufficiently high temperature, it becomes incandescent (emits light), the filaments used in the first electric lamps were made of carbon, but they are now made of a metal (tungsten), which has considerably less resistance than carbon and is more efficient in producing light.

14 Chemical Properties of Carbon

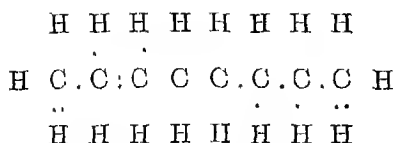
Carbon combines only very slowly, usually

imperceptibly, with other elements at ordinary temperatures. At higher temperature it combines with many metals to form *carbides*, such as those of calcium, CaC_2 , and iron, Fe_3C . It also combines with several non-metals. The two oxides are the most familiar of these binary compounds. When carbon burns in an adequate supply of air and at a temperature of 1000° or above, carbon dioxide, CO_2 , is produced, a limited supply of air and lower temperatures (up to 500°) favor the production of carbon monoxide, C. The use of carbonaceous materials as fuels depends upon the heat liberated when these oxides (usually carbon dioxide) are formed.

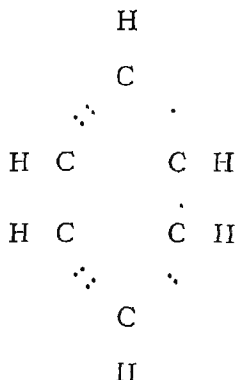


Carbon also unites with sulfur at elevated temperatures to form carbon disulfide (CS_2) and with silicon to form silicon carbide (SiC). It also combines directly with hydrogen to form hydrocarbons (page 117). This reaction is usually catalyzed in order to accelerate its speed.

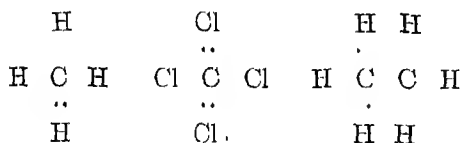
The carbon atom has four electrons in its outermost level and, in keeping with this structure, has a maximum valence of 4. It sometimes has a valence of 2, as in carbon monoxide. This valence indicates that, of the four valence electrons of carbon, two are probably more easily removed from the atom or can otherwise participate in reactions in which they are shared with other atoms more readily. The element usually forms covalent bonds with other elements, however, and positive or negative *carbon ions* never appear in solutions of its compounds. This behavior indicates that carbon does not, ordinarily, lose or gain electrons by transfer; it unites with other atoms by sharing electrons. Since it contains four electrons that may be shared, this number represents its maximum covalence. Two carbon atoms may share electrons with each other. This property gives rise to molecules of carbon compounds in which many carbon atoms may be bound together to form a long chain, as in octane,



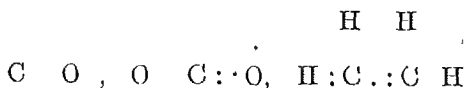
or to form rings, as in benzene,



One, two, or even three pairs of electrons may be shared by a carbon atom with another atom. In methane (CH_4), in carbon tetrachloride (CCl_4), and in ethane (C_2H_6),



the carbon atom shares only one electron pair with each of the atoms with which it is combined. In carbon monoxide (CO), in carbon dioxide (CO₂), and in ethylene (C₂H₄),



it shares two pairs with some atoms and one with others. In acetylene (C₂H₂),



each carbon atom shares three pairs with the other. Compounds such as methane and ethane are said to be saturated, i.e., the combining capacity of carbon is fully satisfied. Ethylene and acetylene are said to be un-

saturated, since extra pairs of electrons between carbon atoms may be used to unite carbon with atoms of hydrogen, chlorine, bromine, iodine, or other elements.

The remarkable tendency of carbon to form covalent linkages — particularly linkages uniting carbon to carbon — is responsible for the extremely large number of compounds of this element.

Hot carbon is an inexpensive and efficient reducing agent. Thus, it reduces hydrogen in the production of water gas from steam, forming carbon monoxide and setting hydrogen free. Its use in metallurgy also depends upon its ability to reduce the metals from their combination with oxygen to the free state.

Review Exercises

- How are the allotropic forms of carbon alike and how are they different?
- How could you prove that a sample of graphite is pure carbon? How does a sample of graphite differ from a sample of anthracite coal?
- How do the different kinds of coal differ? Which kind of coal is best for producing illuminating and fuel gas? Which has the highest and which the lowest heating value?
- Name four kinds of amorphous carbon.
- Explain "destructive distillation" as applied to coal and wood.
- How is graphite prepared? What are four uses of graphite?
- How is gas carbon made? Lampblack? What are their uses?
- How much water at 0° C. could be raised to 100° and changed into steam by burning 10 grams of pure carbon? What volume would the vapor occupy at 100° and 760 mm.?
- Why is coal or wood a better fuel than graphite?
- Describe the action of charcoal in a gas mask.
- What is a carbide? Give three examples.
- How is coke produced from coal? Why is more and more coke being produced in "by-product" ovens rather than in "beehive" ovens, although the latter is the cheaper process?

- 13 Explain the origin of coal. How do you think the natural forms of graphite have been produced?
- 14 How does coal differ in composition from wood?
- 15 What properties of carbon are predictable from its position in the periodic table? What other properties can you add to these?
- 16 How are artificial diamonds produced?
- 17 Refer to pages 150 and 180 for the heats of combustion of carbon and hydrogen. Using the data in Table 14, calculate the heating value in calories of one pound of bituminous coal. Convert calories to B T U and compare your result with the heating value of Table 14. Why are they not the same?
- 18 What was the approximate volume of the uncut Cullinan diamond?
- 19 What weight of graphite would occupy approximately the same volume as the Cullinan diamond?
- 20 What (standard) volume of carbon dioxide is produced when 1 g of diamond burns? 1 g of graphite?

References for Further Reading

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- Gas Masks. *Chem and Met Eng*, **46**, 136, 143 (1939); *Ind and Eng Chem*, **11**, 93, 281, 402, 1105 (1919).
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THE OXIDES AND OTHER SIMPLE COMPOUNDS OF CARBON

Carbonic acid (carbon dioxide) extinguishes burning substances of all kinds. Bodies, when immersed in it, do not cease to burn from a want of oxygen only. It exerts a positive influence in checking combustion, as appears from the fact that a candle cannot burn in a gaseous mixture composed of four measures of atmospheric, and one of carbonic acid.

A CHEMISTRY TEXTBOOK OF 1828

1. Introduction

This chapter deals with the oxides, carbonic acid and its salts, and certain important binary compounds of the element such as CCl_4 and CS_2 . Organic compounds, all of which contain carbon, will be discussed in later chapters.

CARBON MONOXIDE

2. Production by Combustion

Mixed with carbon dioxide, nitrogen, water vapor, and other gases, carbon monoxide is produced whenever carbon or carbonaceous materials are burned in a limited supply of air. Thus, every stove or furnace may act as the producer of a mixture of gases containing carbon monoxide if combustion is not complete. The exhaust from automobile engines always contains this oxide, the amount ranging up to 10 or 12 per cent. Although the danger arising from this source of the very poisonous gas (CO) is well known, several persons die each year from breathing the fumes that escape from motors operated in closed garages. Others die from poisoning produced by inhaling carbon monoxide that escapes into

the living quarters of houses from faulty stoves and furnaces.

The conditions which result in the production of carbon monoxide in an ordinary coal stove or furnace are shown in Figure 154. Air enters the stove at the bottom and,

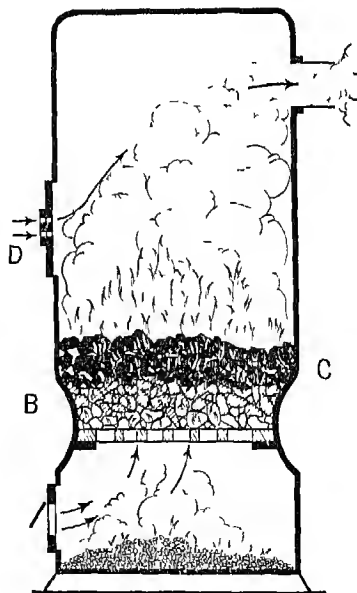
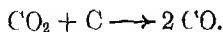
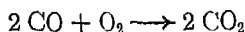


Figure 154 The Combustion of Coal
At B, carbon burns to form CO_2 ; at C, carbon dioxide is reduced by hot carbon to CO .

passing through the grate-bars, converts the carbon in the bottom layer of coal into carbon dioxide. The oxygen of the air may be completely consumed by this reaction. In the middle and upper layers, carbon dioxide reacts with hot carbon, forming carbon monoxide:



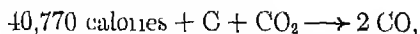
Above the coal, the carbon monoxide may be converted again into carbon dioxide, provided that a further supply of air is admitted through the damper (*D*)



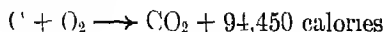
If this damper is closed, the carbon monoxide remains unchanged. If the fumes escape through some leak in the pipe or its connections, serious effects may result because of their poisonous physiological action.

3. Production for Industrial Uses

Carbon monoxide is usually produced commercially by the reaction of carbon dioxide and hot carbon. If air is used to oxidize the carbon to carbon dioxide, before the subsequent reduction to carbon monoxide, the product contains a large percentage of nitrogen. Practically pure carbon monoxide can be prepared by using oxygen to form carbon dioxide instead of air. Oxygen is not well suited for the purpose, however, since the heat which is liberated in the production of carbon dioxide is so excessive that extremely high temperatures result. The temperature can be reduced and a pure product can be obtained if a mixture of oxygen and pure carbon dioxide is passed over the carbon. Since the reaction between carbon dioxide and carbon consumes heat,



this reaction offsets the effect of the oxidation of carbon,



The proportion of carbon dioxide and oxygen may be controlled to give the optimum temperature conditions.

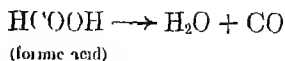
Impure carbon monoxide is produced in the reactions involved in many industrial processes. Among these are the blast furnace reactions in the reduction of iron, in which large quantities of carbon monoxide escape from the top of the furnaces in a mixture that also contains large percentages of carbon dioxide and nitrogen, a little hydrogen, and other gases. This mixture is called *blast-furnace gas* and is used as a cheap but low-grade fuel.

Producer gas, also a cheap fuel, is produced by blowing a blast of air mixed with steam over hot soft coal, wood, or other carbonaceous material. It contains large percentages of nitrogen (about 50 per cent), hydrogen, hydrocarbons, and some carbon dioxide. Its carbon monoxide content is usually 20 to 25 per cent. Coal of inferior grade can be used to make producer gas, which can then be used as a fuel in place of gasoline in gas engines.

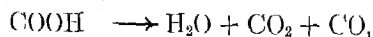
Water gas is produced by the action of steam on red-hot coke. It contains carbon monoxide and hydrogen. This is sometimes an important source of carbon monoxide, particularly in the synthetic production of methyl alcohol. In the reaction involved in this process both carbon monoxide and hydrogen are necessary. Water gas provides both of the required substances, although its composition may be slightly modified to provide the most satisfactory proportions of the two constituents.

4. Laboratory Production

Pure carbon monoxide may be produced in the laboratory by heating formic or oxalic acid,



(formic acid)



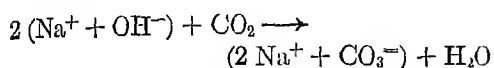
|



(oxalic acid)

or by treating these acids with concentrated sulfuric acid, which extracts water from

them. In the case of formic acid the removal of a molecule of water leaves pure carbon monoxide. In oxalic acid, the withdrawal of the water molecule causes the remainder of the molecule to decompose into a molecule of carbon monoxide and one of carbon dioxide. The former may be recovered by liquefying the carbon dioxide or by passing the gaseous mixture resulting from the decomposition through a solution of sodium hydroxide



Carbon monoxide does not react with sodium hydroxide

5 Properties

Carbon monoxide is a colorless, odorless, and tasteless gas. The absence of odor increases the danger of fatalities resulting from breathing the fumes from automobile exhausts and faulty stoves. Because it is odorless, the presence of the gas is not easily detected. Often it is too late, when the effects of the poisonous gas are detected, for the victim to move into clean air because of his failing motor activity. Carbon monoxide dissolves very slightly in water, is slightly lighter than air (density 0.967 compared to air), and is liquefied with much greater difficulty than carbon dioxide. It condenses at -192° under a pressure of one atmosphere.

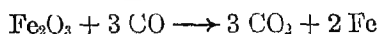
The valence of carbon in carbon monoxide is 2. Since the usual valence of the element is 4, carbon monoxide is a reducing agent. It is not very active at low temperatures. When ignited, it burns in air, with a characteristic blue flame. This flame is often observed above a red-hot bed of coals. Because of its tendency to combine with oxygen, carbon monoxide is useful as a reducing agent in the production of free metals from their oxides.

Formaldehyde and methyl alcohol can be produced from carbon monoxide and hydrogen with the aid of a catalyst and under the proper conditions of temperature and pres-

sure. This oxide of carbon also combines with chlorine to form phosgene, COCl_2 , in sunlight or in the presence of certain catalysts, of which charcoal is an example. The formation of this compound depends upon the valence of 2 which carbon has in carbon monoxide. The presence of two unused electrons in the atom allows carbon to combine with two chlorine atoms, each of which has one electron to share. Phosgene is used in the manufacture of dyes and drugs but is most familiar as one of the poisonous gases used in World War I. Carbon monoxide also unites with some of the metals, forming compounds called *carbonyls*. The carbonyls of iron, $\text{Fe}(\text{CO})_5$, nickel, $\text{Ni}(\text{CO})_4$, chromium, $\text{Cr}(\text{CO})_6$, and cobalt, $\text{Co}(\text{CO})_8$, are typical examples. The carbonyls are unstable, volatile compounds. They are also poisonous. The analysis of mixtures of gases for carbon monoxide depends upon the absorption of the oxide in an ammoniacal solution (containing ammonia) of cuprous chloride. The monoxide reacts with copper forming a type of carbonyl molecule, $\text{Cu}(\text{CO})\text{NH}_3\text{Cl}$. The decrease in volume due to the removal of carbon monoxide in the formation of this compound is a measure of the amount of the monoxide present.

6 Uses

Carbon monoxide is most extensively used as a fuel, usually in such mixtures as water gas, producer gas, and blast-furnace gas. It is also used in the synthesis of methyl alcohol and formaldehyde, and in the preparation of phosgene. It is an extremely important industrial reducing agent, since the reduction of the oxides of many of the metals, such as iron, copper, and zinc, depends upon its tendency to combine with oxygen. In the blast furnace, for example, the principal reducing reaction is



It is also used in the purification of nickel, a process which depends upon the prepara-

tion and subsequent decomposition of nickel carbonyl

7. Poisoning by Carbon Monoxide

Carbon monoxide is the most common poisonous gas. It has been little used in warfare, however, because it is relatively light, having a density slightly smaller than that of air. Because of its small density it does not cling to the ground as heavier gases such as phosgene or chlorine do, but tends to rise. Constant care must be exercised in many peacetime activities, however, against the dangers of this odorless and therefore treacherous poison. Precautions which must be observed in the home and in automobile garages have already been mentioned. The ordinary automobile engine while idling, or when being warmed up, will produce a dangerous proportion of carbon monoxide in a small closed garage in three to five minutes. Explosions resulting from the combustion of finely divided carbonaceous materials, such as coal or flour, always result in the formation of some carbon monoxide. Many of the persons who perish in coal-mine explosions die from the effects of carbon monoxide poisoning, and rescuers upon entering the mine are often overcome from the same cause. A person exposed to air containing one part of the monoxide in 500-750 parts of air for a period of an hour is in danger. An exposure for three to four hours usually results in death.

Birds are sometimes carried by rescue parties after coal-mine explosions. The birds are more sensitive to carbon monoxide than man, their collapse serves as a warning that the gas is present. More dependence is placed upon detection by means of chemical reactions in many places. The most efficient detector, and the one commonly used, consists of a mixture of pumice, iodine pentoxide (I_2O_5), and sulfuric acid. The mixture is called "hoolamite." In the presence of carbon monoxide it develops a green color.

The danger from the poisonous action of carbon monoxide has led to attempts to prepare a gas mask which may be worn for protection by those who must expose themselves to an atmosphere

containing dangerous quantities of the gas. The need has been particularly great on warships, where the gunners are exposed to the large amounts of carbon monoxide liberated in the gun turrets when large guns are fired. The ordinary charcoal-filled masks give no protection against carbon monoxide, which passes through unadsorbed on account of its low density and relatively low critical temperature. Masks have been prepared which contain substances that catalyze the oxidation of the monoxide to the dioxide. The latter is relatively harmless. *Hopcalite* is frequently used for this purpose, it is a mixture of manganous oxide (MnO), cupric oxide (CuO), cobaltic oxide (Co_2O_3), and silver oxide (Ag_2O).

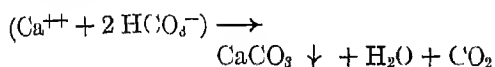
The poisonous physiological effect of carbon monoxide is due to its combination with the hemoglobin, or red coloring matter, of the blood. The function of hemoglobin is the transportation of oxygen from the lungs to the various parts of the body, where it is used in oxidation. To perform this function the hemoglobin forms a relatively unstable compound with oxygen. This compound, which is called oxyhemoglobin, is responsible for the red color of arterial blood. Carbon monoxide also combines with hemoglobin, and since it combines much more readily than oxygen, its presence in inhaled air causes a decrease in the amount of oxyhemoglobin which the blood can form. The compound of the monoxide is moderately stable, and hence the hemoglobin which thus combines is not released very readily. If carbon monoxide continues to be inhaled, the blood loses its ability to absorb and transport an adequate supply of oxygen. Death finally results from the failure of the respiratory organs to function.

CARBON DIOXIDE

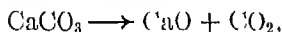
8. Occurrence

Air contains on the average about 3 parts of carbon dioxide per 10,000 parts of air, or about 0.03 per cent, by volume. While this is a small percentage, the total quantity

in the atmosphere is several billion tons. This quantity remains almost constant for several reasons. It is continuously added in the air exhaled from the lungs of animals, the air exhaled by man contains about 4.5 per cent of carbon dioxide. It is also produced by the combustion of fuels and in the decay of all organic materials. The gases from some oil and gas wells contain carbon dioxide and some is present in solution in the waters from certain springs. Hard water usually contains carbon dioxide in the form of the bicarbonates of calcium and magnesium. When these waters are boiled, the bicarbonate ($\text{Ca}(\text{HCO}_3)_2$) is converted to the carbonate, and carbon dioxide is released.



It also occurs naturally in chemical combination in rocks, such as marble, dolomite, and limestone; in trona, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2 \text{H}_2\text{O}$, and in the carbonate ores of some metals. Free carbon dioxide escapes into the air as the product of several chemical reactions which are carried out industrially. The most important of these are (1) the production of lime from limestone,



(2) certain fermentations, such as that of glucose (sugar) to ethyl alcohol,

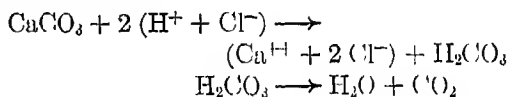


and (3) metallurgical operations involving the reducing action of carbon or carbon monoxide. The most widely used reaction of this kind is the reduction of the oxide-ores of iron in the blast furnace.

The concentration of carbon dioxide in the atmosphere would gradually increase were it not for its removal by other agencies. Some dissolves in rain water and in the surface waters of the earth. Large amounts are removed by plants which use it in the synthesis of starches, sugars, and other substances.

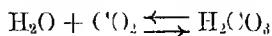
9. Preparation

In the laboratory, carbon dioxide is usually prepared by the reaction of acids, usually hydrochloric, upon calcium carbonate, CaCO_3 . Limestone and marble, which are natural forms of calcium carbonate, are employed instead of chemically prepared calcium carbonate. The generator used for the preparation may be one of the Kipp variety (page 107) or one made from a bottle and a thistle tube (page 106). The reaction is a double decomposition, and calcium chloride and carbonic acid, H_2CO_3 , are formed. The latter is unstable at atmospheric pressure and decomposes into water and carbon dioxide. The dioxide is not very soluble in water and escapes through the delivery tube into the receiver, where it may be collected by the upward displacement of air. It may also be collected over warm water with slight loss.



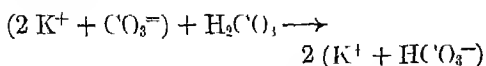
Other carbonates, such as Na_2CO_3 , may be used instead of calcium carbonate. Limestone is less expensive and is generally used, unless a very pure sample of the dioxide is desired.

In this country much of the carbon dioxide used industrially is formed by the combustion of coke, or sometimes coal. The gases that escape from a coal-burning furnace contain nitrogen, carbon monoxide, steam, and many other substances in addition to carbon dioxide. To remove the carbon dioxide, the gases are passed through a tower filled with coke which is sprayed with a solution of potassium carbonate. The carbon dioxide dissolves in the water forming carbonic acid.

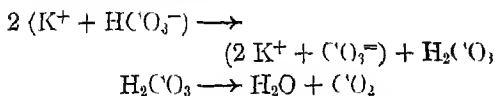


This reaction is reversible, and to aid in the formation of the acid the gases are passed into the tower under pressure. Under these conditions the carbon dioxide dissolves more readily, because the solubility of a gas in a

liquid depends upon the partial pressure of the gas in the space above the liquid. If the molecules are crowded together in this space by increased pressure, more of them will strike the surface and pass into solution than would if the number in this space were smaller. The carbonic acid that is first formed then reacts with the potassium carbonate to form potassium bicarbonate, KHCO_3 .

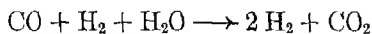


The resulting solution is later removed to another container where it is heated, usually under reduced pressure. Here the reactions proceed in the opposite direction:



Potassium carbonate is formed and may be used over again. Fairly pure carbon dioxide is evolved. This is compressed in steel cylinders. The energy required for compression may be supplied by the combustion of the coke. The pressure in the cylinders is about 900 pounds per square inch.

Carbon dioxide is also produced when hydrogen is prepared from water gas (page 111). It will be remembered that this process for the preparation of hydrogen calls for the passage of a mixture of water gas and steam over a catalyst. The following reaction occurs:



The carbon dioxide is then removed by being dissolved in cold water under pressure. It may be recovered in a fairly pure state by reducing the pressure and heating the solution.

Other sources of industrial carbon dioxide are the decomposition of limestone in preparing lime and the fermentation industries (page 301). This substance is not an expensive commodity because it is a by-product of several industries. Its production

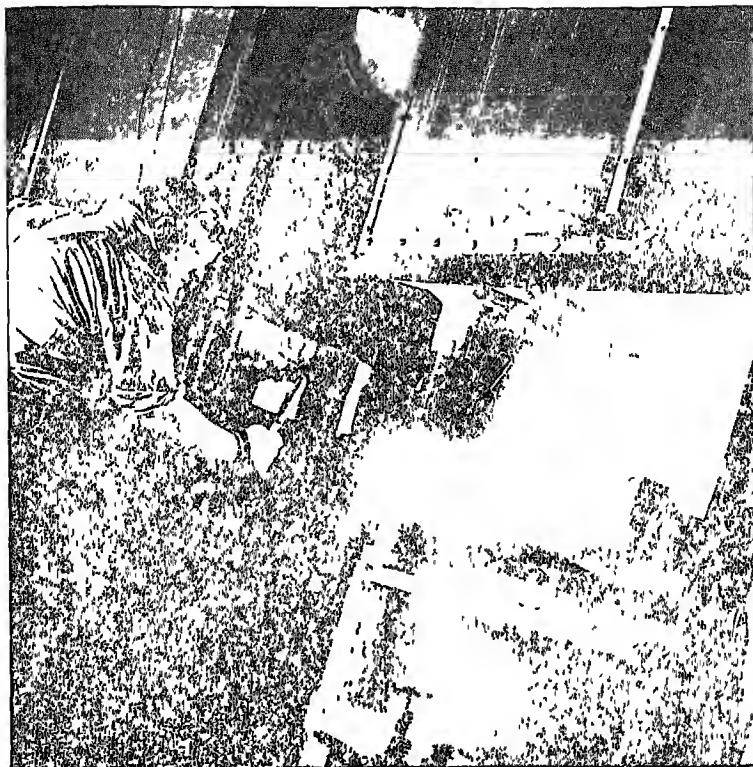
in many cases, as in the manufacture of lime and in the burning of coal to produce heat, so far exceeds the demand that the recovery and purification of the gas is not profitable. Many times more carbon dioxide is allowed to escape into the air than is recovered and purified.

10 Physical Properties

Under ordinary conditions, carbon dioxide is a colorless, odorless gas. Its solubility in water, although greater than that of other gases which we have studied, is not very marked. At 15° and under one atmosphere of pressure, one liter of water dissolves about one liter of the gas. The solubility increases under higher pressures, because of the tendency of carbon dioxide to react with the water, forming carbonic acid. The density of the gas is 1.53 as compared with the density of air. At 20° it is liquefied by a pressure of about 56 atmospheres. Its critical temperature is 31.35° . The carbon dioxide that is sold in steel cylinders is in the liquid state. When the valve of the cylinder is opened, the pressure is reduced and the liquid changes into the gas. If the liquid is allowed to flow out of the cylinder, the cooling that attends evaporation is sufficient to lower the temperature of the liquid to about -79° , where it changes to a white solid. The solid passes directly into the gaseous state (sublimes) without melting, unless the pressure is considerably increased.

11 Dry Ice

Solid carbon dioxide — carbon dioxide snow — is now used as a refrigerant under the trade name of *Dry Ice*. Since it changes directly to a gas that mixes readily with the air, solid carbon dioxide is more desirable than ordinary ice, which melts to form water that must be disposed of. Small paper cartons may be used, therefore, instead of the heavy and cumbersome containers needed for ice. Dry ice does not require the use of salt and sawdust, and lower temperatures can be attained by using much smaller vol-



Courtesy of The Matheson Alkali Works

Figure 155 Blocks of Dry Ice Are Produced in Presses from Pure Solid Carbon Dioxide

umes and weights of this refrigerant than would be necessary if ordinary ice were used. The evaporation of carbon dioxide from the solid requires heat, and the removal of this heat from the surroundings is responsible for the refrigerating action. Dry ice is extensively used for the refrigeration of fruit, meat, and fish and for the preservation of ice cream. A very cold mixture may be prepared by pouring ether, acetone, chloroform, or other volatile liquids upon solid carbon dioxide. With ether or acetone as the liquid, a temperature as low as -80°C can be attained. Mercury is frozen by this mixture, and in it a piece of rubber tubing becomes hard and so brittle that it can be shattered with a hammer.

Solid carbon dioxide can be prepared in the laboratory by allowing the gas to escape from the steel cylinder, in which it is purchased, into a cloth bag. The cylinder is tipped over until

the escape valve is a little lower than the rest of the container. The evaporation of liquid and the expansion of the gas cause heat to be absorbed, and the temperature is reduced to a point where some of the liquid carbon dioxide changes to the solid. This may be removed from the inner walls of the bag. A piece of carbon dioxide snow held in the palm of the hand does not come into contact with the skin. If it did so, considerable danger might be involved in its handling. The solid is always covered by a layer of gas. If the snow is squeezed between the fingers, however, very painful "frostbites" will result.

12 Chemical Properties

Carbon dioxide is relatively stable. Only about 2 per cent decomposes to form carbon monoxide and oxygen at a temperature of 2000°C . Because of its stability it does not often act as an oxidizing agent, although it consists of almost 73 per cent of oxygen.

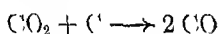
It is reduced by a few vigorous reducing agents. Very active metals such as sodium and magnesium will remove its oxygen (at high temperatures) very readily. An ignited strip of magnesium ribbon will continue to burn in an atmosphere of carbon dioxide and will even reduce the solid



Sodium reduces the dioxide to carbon and forms sodium carbonate

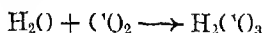


The most familiar reducing agent for carbon dioxide is carbon

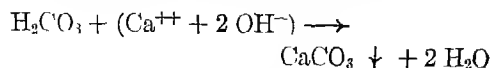


This reduction occurs whenever carbon dioxide (in the absence of oxygen) comes into contact with hot carbon (page 298). Carbon dioxide possesses no reducing properties, since it contains a carbon atom with a valence of 4, which represents the maximum combining capacity of the element.

The chemical characteristics of carbon dioxide show that carbon is a non-metal. The aqueous solution of the dioxide contains some carbonic acid, H_2CO_3 . This is produced by the reaction

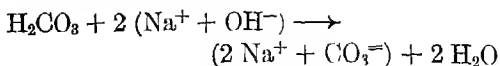


In the presence of at least traces of water, the dioxide reacts with oxides of metals to form carbonates. It forms the same compounds when it reacts with the hydroxides of the metals. Thus, when carbon dioxide is bubbled into a solution of lime water ($\text{Ca}(\text{OH})_2$), a part of the gas dissolves, forming carbonic acid. This then reacts with the calcium hydroxide as follows



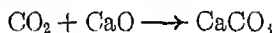
Calcium carbonate is only slightly soluble and precipitates from the solution. This reaction is often used as a *qualitative test* for the presence of carbon dioxide. Barium hydroxide ($\text{Ba}(\text{OH})_2$) is sometimes used in

place of calcium hydroxide, because it is much more soluble and a more concentrated solution can be prepared. This permits the detection of smaller quantities of carbon dioxide. When the gas is passed into a solution of sodium hydroxide, sodium carbonate is produced



The product in this case is soluble, hence no precipitate forms. Sodium hydroxide cannot be used, therefore, in the place of calcium hydroxide in testing for carbon dioxide.

When quicklime (CaO) is exposed to the air it is "carbonated," that is, the carbon dioxide in the air converts the oxide of calcium into calcium carbonate



A trace of water must be present. Hence, we may conclude that the reaction occurs between calcium hydroxide and carbonic acid. The water is released again when these two substances react. Lime-plaster and mortar contain calcium hydroxide (or slaked lime) mixed with enough water to form a plastic mass. The hardening and "setting" of plaster results from the loss of water by evaporation and, more particularly, from the reaction between calcium hydroxide and carbon dioxide to form calcium carbonate.

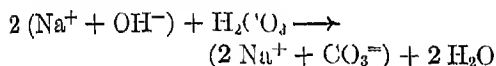
13. Carbonic Acid and the Carbonates

Carbonic acid, H_2CO_3 , is an unstable compound. The solution formed by bubbling carbon dioxide into cold water at one atmosphere of pressure contains only small amounts of the acid, but larger amounts are formed if the gas is dissolved in the liquid under high pressures.

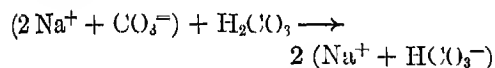
The aqueous solution has the properties of a very weak acid. In this respect it compares very unfavorably with hydrochloric, sulfuric, and even acetic, a relatively weak acid which we find in vinegar. The stronger acids have a very sour taste and immediately

turn blue litmus paper to a sharp red color. A solution of carbonic acid, on the other hand, is only very mildly "acid" in taste and slowly turns blue litmus to a faint pink. The biting taste of "soda water" is due to this acid. The name "soda water" is associated with soda (sodium carbonate) from which the carbon dioxide used to prepare *carbonated water* was once derived by the action of an acid. Beverages are now carbonated by carbon dioxide that is purchased in steel cylinders.

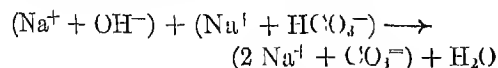
The reaction of carbonic acid with a base, such as sodium hydroxide, may produce sodium carbonate or sodium bicarbonate, depending upon the relative amounts of base and acid available for the reaction. In the presence of an excess of the base, sodium carbonate is produced:



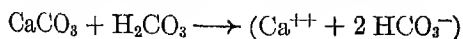
When an excess of carbon dioxide is passed into the solution, sodium bicarbonate is produced:



To assure the preparation of sodium carbonate, a solution of sodium hydroxide is *saturated* with carbon dioxide. This forms pure sodium bicarbonate. The resulting solution is then mixed with an equal volume of a new sodium hydroxide solution, containing the same quantity of sodium hydroxide as the first solution. In this mixture sodium bicarbonate is converted into the carbonate by the following reaction:



"Ground" water contains small amounts of carbonic acid in solution. When this comes into contact with limestone in the earth, the following reaction occurs:

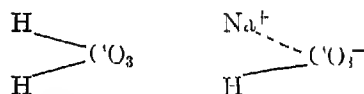


The calcium bicarbonate, $(\text{Ca}(\text{HCO}_3)_2)$, which is relatively soluble, is carried away in solution. This is the manner in which "soft" water most often becomes "hard." It is also one cause of the development of cavities and channels in deposits of limestone rocks.

14 Dibasic Acids and Acid Salts

Carbonic acid is a *dibasic acid*. This statement means that a molecule of the acid contains two replaceable atoms of hydrogen — liberates two protons for reactions with bases, two moles of sodium hydroxide, for example, are required to react completely with one mole of the acid. A *monobasic acid*, such as hydrochloric acid, contains only one replaceable atom of hydrogen per molecule, a *tribasic acid*, such as phosphoric acid, H_3PO_4 , contains three.

The reaction of a molecule of carbonic acid with one hydroxyl ion from sodium hydroxide removes only one hydrogen ion, or proton, from the acid and forms sodium bicarbonate, $\text{Na}^+\text{HCO}_3^-$:



The second hydrogen ion may be removed if another hydroxyl ion from sodium hydroxide is available, i.e., if one gram-molecular (or gram-formula) weight of sodium hydroxide is added for each gram-molecular (or gram-formula) weight of sodium bicarbonate.

A salt in which only a part of the replaceable hydrogen of an acid has been neutralized is an *acid salt*, it can still act as an acid by liberating the remainder of the replaceable hydrogen to react with bases.¹ Sodium bicarbonate, therefore, may be called *sodium acid carbonate*. Other acid salts are sodium

¹ Not all the atoms of hydrogen in every acid are replaceable, not all of the hydrogen atoms in a molecule of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, for example, can react with a base. Only one of the four atoms of hydrogen in a molecule of this acid can do so, and it is for this reason that the formula is not written as $\text{C}_2\text{H}_4\text{O}_2$ or $\text{H}_4\text{C}_2\text{O}_2$.

bisulfate (or sodium hydrogen sulfate, NaHSO_4 , monosodium (dihydrogen) phosphate, NaH_2PO_4 , and disodium (monohydrogen) phosphate, Na_2HPO_4

15 Uses of Carbon Dioxide

We have already mentioned the use of carbon dioxide in the preparation of soda water and in refrigeration. More than 25,000 tons are used annually in this country in producing soft drinks, which are solutions of carbon dioxide under a pressure of about four atmospheres, various flavors, sugar, and sometimes other acids such as citric.

Carbon dioxide is also used to extinguish fires. One of the familiar types of fire extinguisher depends upon the properties of the dioxide. The extinguisher (Figure 156) contains a solution of sodium bicarbonate. A bottle containing sulfuric acid is held in place near the top. Until required for use the container is kept in an upright position. To use it the cylinder is inverted, and the stopper then drops out of the bottle containing the acid. The following reaction takes place

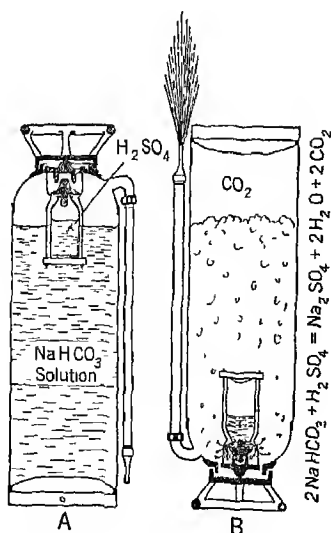
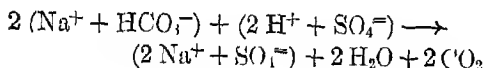
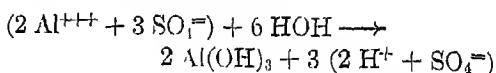


Figure 156 Fire Extinguisher

Considerable pressure develops in the container, and the solution becomes saturated with the dioxide. The pressure forces the solution out through the nozzle. The carbon dioxide accompanying the stream of solution, and also that escaping from it as the pressure is reduced, extinguishes the fire, because it excludes the air and thus prevents the continuation of combustion. The water in the solution that issues with the gas also helps to extinguish the fire by exerting a cooling effect.

The use of another widely used extinguisher is shown in Figure 157. When inverted this extinguisher produces a stream of foam containing carbon dioxide. The inner container of the extinguisher contains a solution of alum or aluminum sulfate. The outer cylinder contains a solution of sodium bicarbonate and lye (sodium hydroxide). The aluminum sulfate reacts with water to form sulfuric acid and aluminum hydroxide



The aluminum hydroxide forms a gelatinous precipitate. When the cylinder is inverted, the two solutions are mixed, and the acid reacts with sodium bicarbonate, liberating carbon dioxide. This gas and the aluminum hydroxide form a froth or foam which is stabilized, or made more nearly permanent, by the presence of the lye. The pressure developed within the extinguisher forces the mixture out of the container. This device is especially useful in fighting fires from burning oil. Such fires are difficult to extinguish with water, because the fire is largely in the vapors above the surface of the oil. The water sinks, floating the oil on top of it. The foam, on the other hand, flows over the surface of the oil, effectively blanketing it. Because of the stable nature of the foam, the carbon dioxide is not carried away from the place of the fire by convection currents. The latter difficulty is one that decreases the usefulness of the extinguisher described in the preceding paragraph.

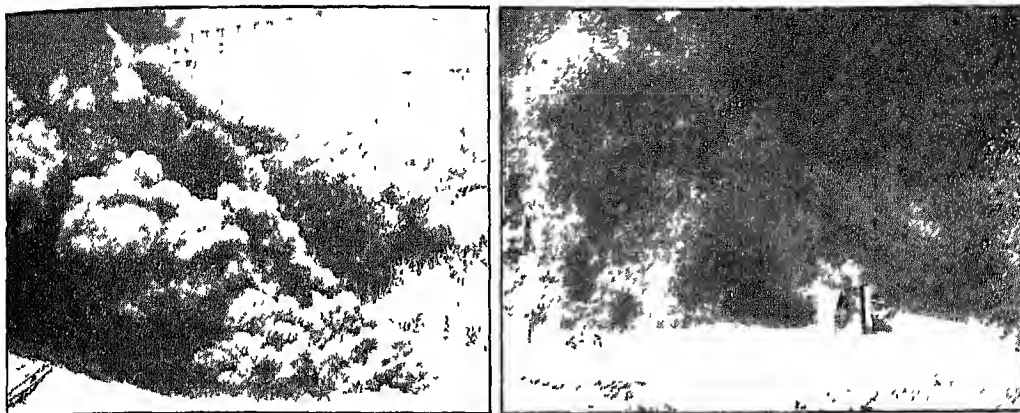


Figure 157 The Use of Firefoam
At left, burning oil, at right, after the use of Firefoam

Carbon dioxide is used extensively in the manufacture of sodium bicarbonate (baking soda). It is also used in the manufacture of white lead, which is an important part of many paints.

Carbon dioxide is mixed with the oxygen that is administered to persons suffering from impairment of the respiratory organs in diseases like pneumonia and in cases of asphyxiation. The presence of carbon dioxide stimulates the nerve centers that control respiration. The normal exhaled air from the human lungs contains between four and five per cent of this substance.

Carbon dioxide is responsible for the leavening of dough in baking. It is liberated in the dough by the action of yeast that promotes the fermentation of sugar, by the reaction of soda (sodium bicarbonate) and the lactic acid of sour milk, or by the reaction of the ingredients of baking powder. The different kinds of baking powder contain baking soda and an acid salt such as potassium hydrogen tartrate, $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$, or monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, or a substance such as sodium aluminum sulfate, $\text{NaAl}(\text{SO}_4)_2$, which reacts with water to form an acid. When the powder is mixed with water, in dough or elsewhere, the bicarbonate ion of the baking soda reacts with hydrogen ion to form carbonic acid, which then decomposes to liberate carbon dioxide. The

expansion of the gas during heating and its tendency to escape, just as bubbles of gas escape from water, cause the dough to "rise" and render the baked product more porous than it otherwise would be.

One of the new uses for carbon dioxide is in blasting. The liquid is placed in a steel cylinder under about 900 pounds of pressure per square inch. Placed in the cylinder with it, is an easily ignited mixture, which by releasing heat vaporizes the liquid, thus greatly increasing the pressure (30,000 pounds or more). The cylinder is fitted with a special cap that is blown off when the pressure becomes great enough, and the release of the gas at this high pressure has the same effect as the explosive decomposition of an unstable compound.

16 Carbon Disulfide

Carbon disulfide, CS_2 , is the sulfur compound of carbon that corresponds to carbon dioxide. It is produced when sulfur vapor is passed over hot carbon. We may think of the carbon as burning in an atmosphere of sulfur, just as it usually burns in an atmosphere of oxygen or air. In order to prevent the combustion of both carbon and sulfur by oxygen, the production of carbon disulfide must be carried out in the absence of air. It is produced in an electric furnace of the type shown in Figure 158. Sulfur and



Figure 158 Production of Carbon Disulfide in the Electric Furnace

Charcoal is fed in at C and sulfur at A and O

coke are fed into the furnace continuously. The sulfur is vaporized, and the carbon is heated to the required temperature by the heat which is liberated by the passage of the electric current between the two electrodes. The disulfide is volatile and distills as rapidly as it is formed. The vapor is passed from the top of the furnace into a condenser.

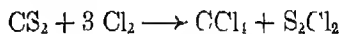
The product has a yellow color because of dissolved sulfur, and an unpleasant odor, which is not that of carbon disulfide but of traces of impurities. The pure substance is colorless and has no disagreeable odor. It is about one and one-fourth times as heavy as water. It does not mix with water, has a high index of refraction, evaporates readily, and therefore has a high vapor tension at ordinary temperatures. The boiling point is 46.3°C . at 760 mm. The vapor has a very low kindling point, a glass rod that has

been heated to a moderate temperature will ignite the vapor if the rod is held an inch or two above the surface of the cold liquid. The substance is poisonous.

Carbon disulfide is used commercially as a solvent for rubber, phosphorus, waxes, gums, sulfur, and fats. The sulfur solution finds some use as a medium for the vulcanization of rubber. Carbon disulfide is also used as a solvent for resins in the manufacture of varnishes and lacquers. It is one of the essential substances in the manufacture of cellophane and is used, in a similar manner, in one of the well-established processes for the manufacture of rayon. The heavy, poisonous vapors that are produced when the liquid evaporates are used to kill weevils in grain and to kill moths, mice, rats, woodchucks, and other small animal pests. Since it is a solvent for fat and grease, it might be used as a dry-cleaning agent if it were not poisonous and inflammable.

17 Carbon Tetrachloride

This substance is well known because of its use in fire extinguishers and in dry cleaning. It is produced by treating carbon disulfide with dry chlorine.



Iodine is used as a catalyst of this reaction. Sulfur monochloride, S_2Cl_2 , boils at 138° and carbon tetrachloride at 77° , hence the two products of the reaction can be separated by fractional distillation. Sulfur monochloride is used to some extent as a solvent for sulfur, and the solution is used sometimes in the vulcanization of rubber. Carbon tetrachloride is also prepared on a small scale by the prolonged action of pure chlorine upon methane, CH_4 , in the sunlight.

The vapor of carbon tetrachloride is considerably heavier than air and is not combustible. For these reasons, and also because the liquid is readily volatile, carbon tetrachloride is used to extinguish fires. The ordinary, small fire extinguisher contains a mixture of carbon tetrachloride and other

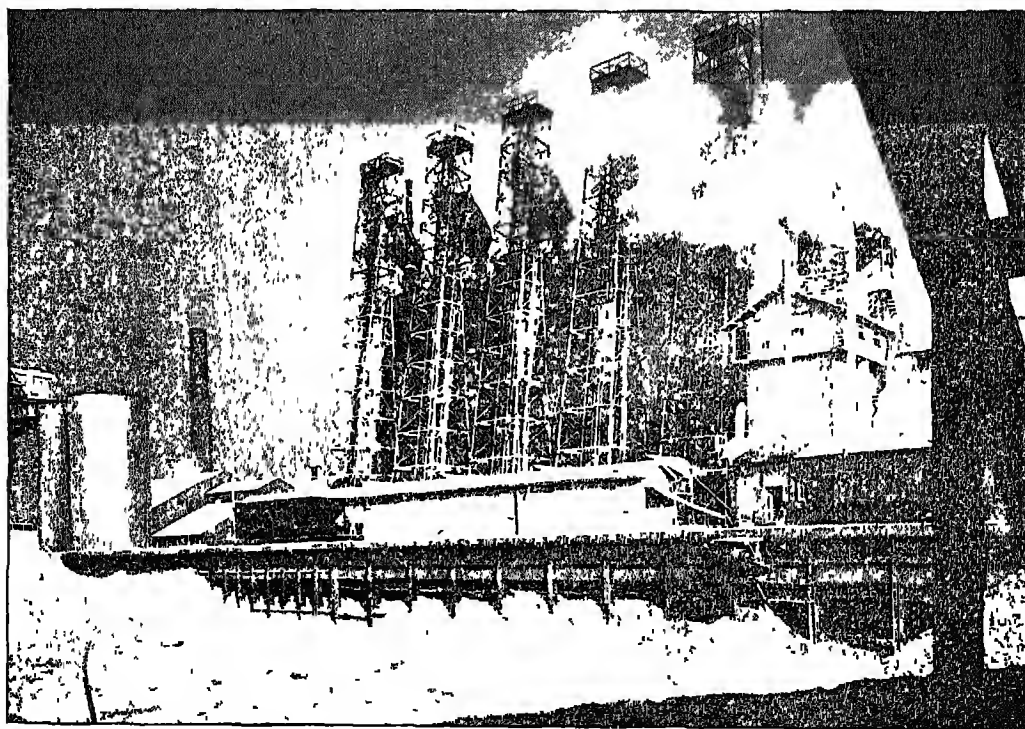
substances. A stream of the liquid is forced through the small outlet at the bottom of the cylinder and played about the base of the fire. The liquid volatilizes, providing a blanket of non-inflammable gas, which excludes the air from the burning material. This type of extinguisher is somewhat more efficient in fighting oil fires than the ordinary extinguisher that uses a mixture of carbon dioxide and water, because carbon tetrachloride mixes with the oil instead of sinking to the bottom as water does.

Some of the liquids used in dry cleaning consist of a mixture of carbon tetrachloride and gasoline or naphtha. The use of carbon tetrachloride for cleaning depends upon its properties as a solvent for grease and oils. The mixture containing gasoline or other hydrocarbons is less expensive than pure carbon tetrachloride and has the advantage, over gasoline, of being difficult to ignite. As much gasoline as possible (about 40 per cent)

is used without producing a mixture which will form vapor that is easily ignited. Carbon tetrachloride is also used as a solvent for grease in cleaning wool, and as a solvent for vegetable oils in the extraction of oils from crushed seeds of various kinds. The tetrachloride is recovered by distillation, and the last traces are removed by blowing steam through the oil.

Carbon tetrachloride has a limited use in medicine in the destruction of parasites, such as hookworm, which may be inhabitants of the alimentary canal. It is also used as a fumigant to kill insects, upon which it acts as a poison.

On the whole, carbon tetrachloride is characterized by inactivity. It is a typical chloride of a non-metal and as such differs greatly from the chlorides of the metals. The latter are conductors of the current both in the fused state and in their solutions. Carbon tetrachloride is a non-conductor.



Courtesy of Pittsburgh Plate Glass Company

Figure 159 Limestone is Hoisted by Elevators to the Tops of Kilns in Which it is Converted into Carbon Dioxide and Lime.



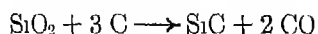
Courtesy of Air Reduction Sales Company

Figure 160. Dry Ice Being Used for Refrigeration

The carbon and chlorine atoms in the molecule are united by shared pairs of electrons (covalences), while the salts of the metals are ionic compounds.

18. Silicon Carbide

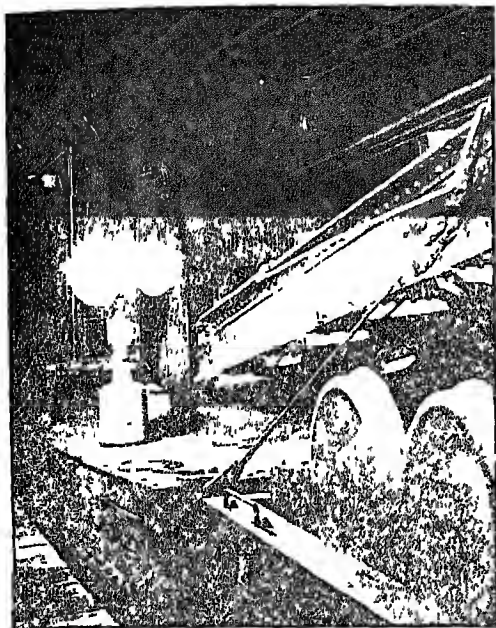
When a mixture of sand and powdered coke is heated to a temperature of about 3000° , the following reaction occurs.



Silicon carbide (SiC), although sold under other names, is best known as *Carborundum*, a trade name given to it by Acheson, who first prepared the substance in 1891. Carborundum is made in an electric furnace in which air is excluded. The furnace is built up of fire brick each time it is used. The

charge consists of a mixture of powdered coke, sand, sawdust, and salt. The sawdust makes a more porous mass and aids in the escape of carbon monoxide, the salt aids in the removal of iron by forming volatile ferric chloride. A cross-section of the furnace and its charge is shown in Figure 162. A core of pure carbon, perhaps graphite, serves as a conductor. The resistance encountered by the current causes the liberation of heat and the central portion of the charge becomes white-hot. The portion of the charge next to the core is converted into crystals of silicon carbide (Figure 162).

Silicon carbide is used principally for grinding-stones, polishing powders, and other forms of abrasives. It will scratch glass and is almost as hard as diamond.

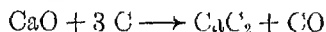


Courtesy of Air Reduction Sales Company

Figure 161. Carbide Lights Used for Night-time Work

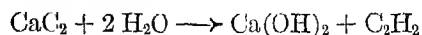
19. Calcium Carbide

This is an important compound of carbon and the metal, calcium. It is produced by heating a mixture of lime and coke in an electric furnace. The walls of the furnace are made of brick, and the charge is poured around large carbon electrodes. Lime reacts with carbon to form calcium carbide and carbon monoxide



At the temperature which is attained in the furnace, the carbide melts and flows out through an outlet in the bottom of the furnace. Since electrical energy is required in the process, plants for producing carbide are located at places where electricity can be produced most economically, as at Niagara Falls and Muscle Shoals (Alabama). The product usually contains coke and other impurities and is gray in color. It is supplied to the market in rather soft, porous lumps. The pure substance is crystalline and transparent.

Calcium carbide reacts with water to form calcium hydroxide and the combustible gas, acetylene (C_2H_2)



Bicycle lamps may be lighted by burning acetylene. In the early days of the automobile, the head lamps were lighted in the same manner, and before the day of the automobile, vehicles were sometimes equipped with lamps which used acetylene. The children of a generation or two ago used carbide to supply the acetylene that was burned to provide illumination in their magic lanterns. The same source of illumination often served in homes and in shops. This, of course, was before the widespread use of the electric light. Acetylene is still produced for such uses, to some extent. The gas is forced under pressure into steel cylinders containing a porous material mixed with acetone, in which acetylene is soluble. Large quantities of the gas are thus compressed in a small space, stored in this manner, acetylene is safe, although the pure liquid is dangerously unstable. Acetylene is now an important substance because of its use in the synthesis of many organic compounds. It is also used in oxyacetylene welding (page 73).

Calcium carbide reacts with nitrogen under certain conditions to form calcium

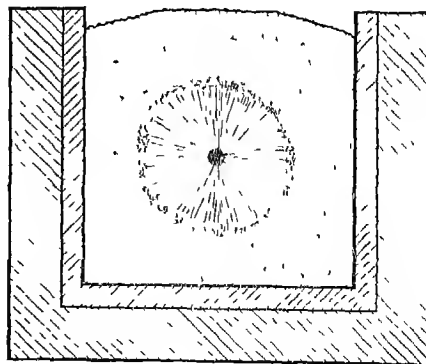
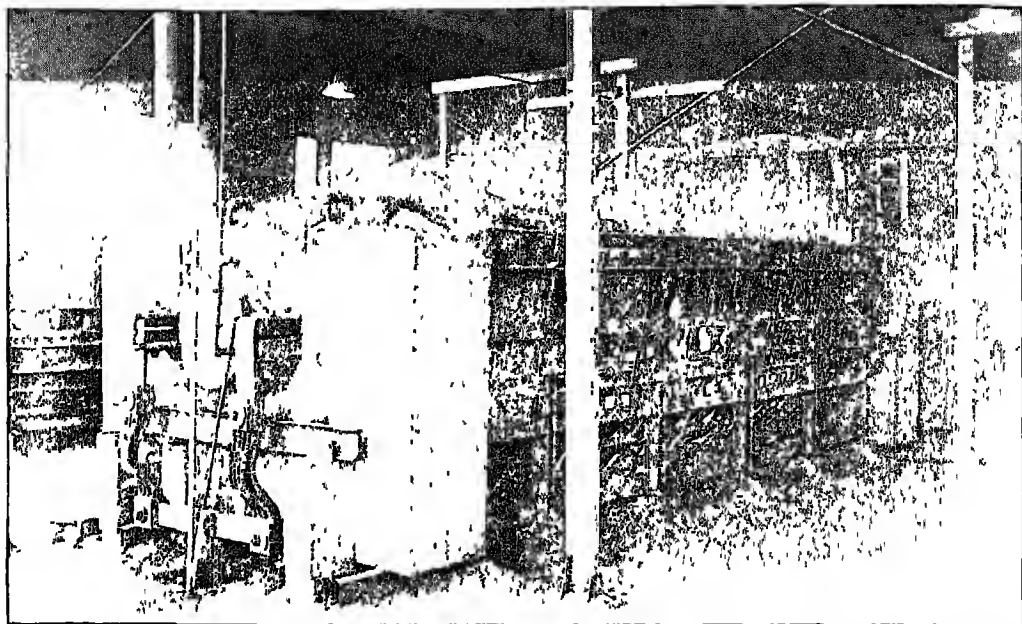


Figure 162. Cross Section of a Silicon Carbide Furnace

The carbon core is surrounded by crystals of silicon carbide



Courtesy of Norton Company

Figure 163 Resistance Type of Electric Furnace in which Sand and Coke are Converted Into Silicon Carbide

cyanamide, CaCN_2 . This substance is important because of its use in fertilizers, and because it may be made to react with steam to form ammonia and with sodium chloride or with sodium carbonate and carbon to form sodium cyanide, NaCN .

Review Exercises

- 1 Explain how carbon monoxide is produced in a stove or furnace
- 2 How would you determine whether a sample of gas is carbon monoxide or carbon dioxide?
- 3 Why is carbonic acid called a dibasic acid?
- 4 What volume of carbon dioxide, at 20° and 760 mm, can be produced (1) by heating 100 g of CaCO_3 , (2) by the fermentation of 100 g of glucose, (3) by burning 100 g of carbon, and (4) by heating 100 g of potassium bicarbonate?
- 5 What are the names and some of the uses of each of the following carbon compounds: NaHCO_3 , CaCO_3 , CaCN_2 , Na_2CO_3 , C_2H_2 , SiC , CCl_4 , COCl_2 , HCOOH , and CaC_2 ?
- 6 Suggest one reason why carbon forms more compounds than any other element
- 7 What weight of calcium carbonate could be converted into calcium bicarbonate by 10 liters (standard conditions) of carbon dioxide, assuming that 10 per cent of the carbon dioxide is not used in the reaction?
- 8 What weight of calcium carbonate is precipitated (0.0013 g dissolves in 100 ml at 18°) when one liter of carbon dioxide (at 0° and 760 mm) is completely absorbed in one liter of a solution containing an excess of calcium hydroxide (at 18°)?
- 9 What volume of carbon dioxide and water vapor at 100° and 760 mm would be produced by the complete combustion of the acetylene which is made when 5 g of calcium carbide reacts with an excess of water?
- 10 Why is carbon dioxide absorbed to a greater extent by a solution of sodium carbonate than by pure water?
- 11 How are the chloride and sulfide of carbon different in properties and structure from the corresponding compounds of the metals?
- 12 Identify or explain water gas, blast-furnace gas, producer gas, phosgene, dry ice, soda water, acid salt, baking powder, and Carborundum
- 13 Suggest one reason why carbon monoxide,

although very poisonous, has never been used as a poisonous gas in war

- 14 What is the loss in heating value if all the carbon in a ton of coke is allowed to escape up the chimney as carbon monoxide? Assume that the coke is pure carbon
- 15 A fire extinguisher contains 25 liters of a solution in which there is 10 g of sodium bicarbonate per 100 ml. of solution. What (standard) volume of carbon dioxide can be produced from the contents of the extinguisher?
- 16 Carbon disulfide burns to form carbon dioxide and sulfur dioxide, SO_2 . What (standard) volume of oxygen is required for the combustion of one gram-molecular weight of carbon disulfide?

Carbon Dioxide *Ind. and Eng. Chem.*, **22**, 140, 437, 1086, 1186 (1930), **24**, 613 (1932), **27**, 1305, 1452 (1935), **29**, 632 (1937), *Chem. and Met. Eng.*, **28**, 5 (1923), **37**, 416 (1930), **38**, 136, 270 (1931), **39**, 433 (1932), **40**, 250 (1933), *J. Chem. Ed.*, **5**, 1321 (1928), **7**, 151, 403, 637 (1930), **9**, 1503, 1523 (1932)

Carbon Disulfide *J. Chem. Ed.*, **8**, 867 (1931)

Carbon Monoxide *Ind. and Eng. Chem.*, **20**, 564 (1928), **21**, 389 (1929), **22**, 1096 (1930), **29**, 495 (1937), *Chem. and Met. Eng.*, **30**, 824 (1924), **43**, 590 (1936)

Carbon Tetrachloride *Chem. and Met. Eng.*, **43**, 313 (1936)

Fire Extinguishers *J. Chem. Ed.*, **9**, 1503 (1932)

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THE ATMOSPHERE

It appears from some recent experiments of Mr. Perkins that air becomes liquid under a pressure of 2000 atmospheres. This requires confirmation, if true, it is probable that pure oxygen and nitrogen gases may also be liquefied by the same degree of compression.

A CHEMISTRY TEXTBOOK OF 1828

1 Introduction

The term *atmosphere* refers to the mixture of gases surrounding the earth. Its total weight is about 5.7×10^{16} tons. This mixture is also commonly called *air*, although the latter term is often used in referring to a small part of the atmosphere. Thus, we usually speak of the air in a container instead of the atmosphere. Air was regarded by the ancients as an element, and until the latter part of the eighteenth century, it was thought to be the only gaseous form of matter. When oxygen and hydrogen were discovered, they were thought to be special kinds of air, hydrogen was called "inflammable" and oxygen "dephlogisticated" air. The experimental work of Scheele, Priestley, Black, Rutherford, and Lavoisier, during the late eighteenth century, provided the background for Lavoisier's explanation of air as a mixture of oxygen and nitrogen, or azote, as it was first called. During the last decade of the nineteenth century, Lord Rayleigh and Sir William Ramsay discovered argon (1894), and Ramsay (with Travers) discovered neon, krypton, and xenon. Ramsay showed that these inert gases, too, are constituents of the atmosphere. He also found traces of helium, the lightest of these gases. In addition to the elements mentioned above, the air contains water vapor, carbon dioxide,

traces of hydrogen, dust, and other more or less accidental substances.

This chapter deals with all the components of the atmosphere except oxygen, which was discussed in Chapter 5, and nitrogen, to which special attention will be given in Chapter 30.

2 Composition

The percentages of the various substances in the air vary greatly with the height above sea level at which the sample of air is collected.

The following table represents the average composition at sea level.

TABLE 15
Composition of the Air, by Volume

Component	Percentage
Nitrogen	78
Oxygen	21
Water vapor	Varies greatly
Argon	0.94
Carbon dioxide	0.03–0.04
Hydrogen	0.01 or less
Neon	0.0012
Helium	0.0003
Krypton	0.00005
Xenon	0.000006
Average density, 1.29 g per liter, standard conditions	

We cannot obtain definite information about the composition of the extreme upper limits of the atmosphere, but it appears likely that the percentages of oxygen, argon, and carbon dioxide decrease gradually with increasing altitude. The relative amount of nitrogen probably increases slightly at first and then decreases until at an altitude of about 50 miles, it is thought, the percentage of nitrogen is very small, probably about 2 per cent. The percentage of hydrogen is thought to increase slowly for the first 30 miles and then to increase rapidly until in the extreme upper parts of the atmosphere it is practically the only substance present.

The pressure of the atmosphere decreases from 760 mm. at sea level to about 40 mm. at ten miles and about 0.1 mm. at thirty miles. The pressure is only about 400 mm. at a height of 15,000 feet. Airplanes can ascend to heights in excess of 40,000 feet. Because of the decreased pressure at that altitude the concentration of oxygen is not sufficient to form explosive mixtures with the "gas" in the cylinders of the engine. To overcome this difficulty a supercharger is used—a device for utilizing the exhaust of the engine in operating a compressor, which feeds air to the engine at a pressure of one (sea level) atmosphere.

Near the earth's surface small amounts of many other different substances may sometimes be found in the air. These are the products of the decay of organic material, of oxidation, of volcanic action, and of industrial activities. They include such substances as ammonia, sulfur dioxide, hydrogen sulfide, and carbon monoxide. Traces of hydrogen peroxide and ozone are also usually present, while living forms of matter are represented by bacteria, yeast cells, and the spores of molds and fungi. Bread left in the air soon shows growths of molds which start from germinating spores that settle out of the air upon the bread. Bacteria and yeast cells are carried by the air and are responsible for the processes of putrefaction and fermentation. In order to protect food materials against these attacks, the speed of the changes which they produce may be slowed down by refrigeration. The organisms may be killed by heat and the materials may then be canned or otherwise sealed to prevent the entrance of other bacteria from

the air. Preservatives may be added which kill the organisms or otherwise prevent their destructive action. Among the preservatives sometimes used are sodium benzoate in catsup, salt in meats, vinegar in pickles, and concentrated solutions of sugar in jams.

3. Air as a Mixture

Even after the discovery that air contains more than one substance and that it cannot, therefore, be an element, there was some doubt concerning its exact nature. The composition, especially as regards its two major components, oxygen and nitrogen, appears to be approximately constant. For this reason there might be some cause to suspect that air is a compound and that the proportions of oxygen and nitrogen are in accordance with the law of definite proportions. We know, however, that the various substances found in the air are only parts of a mixture. This fact can be demonstrated in many different ways.

(1) The composition of air is not definite. The percentages of some of the substances which are always present show considerable variations. This is particularly true of water vapor. Even the percentages of oxygen and nitrogen are not absolutely constant. Samples of air collected in different parts of the world and under different conditions contain slightly more or slightly less than 21 per cent of oxygen and slightly more or slightly less than 78 per cent of nitrogen. The percentage of oxygen is higher in the open fields and in the woods than in cities. In a certain large American city, for example, the percentage of oxygen (average of about fifty analyses) is 20.95 per cent, while the average percentage in the mountains of Scotland is 21.18. The great variations in the composition of the air with altitude is further proof that air cannot be a compound.

(2) Liquid air does not act as a compound. A pure liquid has a definite boiling point, but liquid air does not. As its temperature rises, the composition of the liquid changes and, hence, its boiling point also varies. Certain parts of the air—water vapor and carbon dioxide—are condensed to liquids and are easily separated long before the main portion is liquefied.

(3) When a pure substance dissolves in water,

or in any other solvent, it does so as a whole. The ratio of the elements composing the substance is the same in the solution as it is in the undissolved state. We find, however, that the nitrogen and oxygen of the air have different degrees of solubility. Water dissolves more oxygen than nitrogen, and as a result the composition of dissolved air is different from that of ordinary air. This would not be true if the oxygen and nitrogen were chemically combined.

(4) Chemical changes are associated with changes in energy. Heat is either liberated or absorbed as a change occurs. Yet when oxygen and nitrogen are mixed at ordinary temperatures and pressures, there is no change that indicates either the liberation or the absorption of energy. This must mean that no compound is produced when these elements are brought together under the conditions that exist in the atmosphere.

(5) Probably sufficient proof that air is a mixture lies in the fact that if air is a compound it is totally unlike any compound containing the two elements (nitrogen and oxygen) that has ever been prepared. The oxygen of the air has the same properties as that which is prepared under conditions which prohibit the presence of nitrogen and all other substances. The only difference appears to be one of concentration. Air is less concentrated with respect to oxygen than a sample of the pure element, because of the large percentage of nitrogen with which it is mixed. The oxygen of the air forms the same oxides, and supports combustion, decay, and other oxidation processes in the same manner as pure oxygen, but it does so at a slower rate.

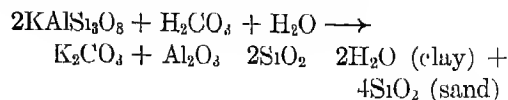
The proportions of the different components of air at one place on the earth are, however, unusually nearly constant. This condition is surprising, when we consider the fact that air is a mixture, and just why it is true cannot be explained entirely satisfactorily. Many factors operate to change the composition of the atmosphere, but they tend to balance the effects of one another. Carbon dioxide, for example, is added to the atmosphere by the respiration of animals and by the combustion and decay of materials containing carbon. These processes also remove oxygen at the same time that they add carbon dioxide. The percentage of

carbon dioxide would gradually increase if certain agencies did not remove it at about the same rate as it is added. Plants absorb carbon dioxide and from it synthesize starch, sugar, cellulose, and the like. During these changes oxygen is released to the air. The life processes of plants therefore tend to balance the effects of animal respiration, combustion, and decay upon the composition of the atmosphere.

The equilibrium conditions that exist between the different components of the atmosphere and their solutions in the water on the earth's surface must also play an important part in maintaining the nearly constant composition of the atmosphere. If a greater than normal concentration of any one of these components appears in the atmosphere, more of that component dissolves until equilibrium conditions are again established.

4. Carbon Dioxide of the Atmosphere

Large amounts of carbon dioxide are removed from the air during chemical changes in various rocks. Thus, a solution of carbon dioxide in water contains carbonic acid, which reacts with limestone and dolomite rocks to form calcium and magnesium bicarbonates. Many millions of tons of the dioxide are removed each year from the air by this and similar reactions. Water containing carbon dioxide dissolved from the air also plays a very important part in the weathering of other kinds of rocks. This is especially true in the decomposition of the feldspars, of which orthoclase (KAlSi_3O_8) is an example. The action of a solution of carbonic acid (H_2CO_3) upon this mineral is shown by the following equation:



Although carbon dioxide is not extremely soluble in water, very large quantities must be removed by dissolving in the water that falls through the air as rain. Some also

dissolves in the waters of rivers, lakes, and the seas, forming a solution in which the carbon dioxide is in equilibrium with the carbon dioxide in the air. If the concentration of this substance in the air should be increased, more of it must dissolve to establish equilibrium again.

Small quantities of the carbon dioxide dissolved in water may also be converted by different forms of aquatic life into calcium carbonate, from which these organisms form their shells and skeletons. The water can then dissolve more carbon dioxide from the air. Most of the carbon dioxide from which these calcium carbonate structures are formed comes, however, from the carbonate carried in solution by river water that empties into the sea. These soluble carbonates are produced directly during the weathering of certain kinds of rocks. But if traced back to its source, the carbon dioxide contained in the substances which river water has in solution will prove to have come from the air. It is said that the quantity of carbon contained in the carbonates found in sedimentary rocks and dissolved in the waters of the earth is some 30,000 times the quantity which exists as carbon dioxide in the atmosphere. If all of it was originally present in the atmosphere — of this we cannot be sure — the percentage of carbon dioxide in the air would necessarily have been much greater than it is now, and the increased quantities of it must have made life, the temperature of the earth, and many natural kinds of chemical changes very different from what they are in our atmosphere. In an atmosphere having such a high percentage of carbon dioxide, the very existence of oxygen-breathing creatures would have been impossible. However, the existence of fossils from the earliest periods, and then similarity to those of later periods in the earth's history indicate that at no time has the atmosphere contained excessive quantities of carbon dioxide.

Several theories have been advanced from time to time concerning the original source of the

carbon dioxide in the air. This subject is of interest because of its bearing upon the question of the origin and development of forms of life. One theory suggests that the carbon dioxide was added to the atmosphere in the beginning by volcanoes, and assumes that carbon originally existed in the earth as graphite. Thus, it is said, was converted into the dioxide by chemical reactions between graphite and the oxides of iron (chiefly magnetic oxide), in which the carbon acted as a reducing agent. Later, when plant life had begun, it was restored to the earth in the form of calcium carbonate deposits, and some of the carbon, in time, became coal. Another theory assumes that carbon dioxide was a constituent of the original atmosphere of the earth. This theory also assumes that no oxygen was present originally and that the oxygen now found in the atmosphere was placed there largely during the Carboniferous period by the action of plants. We cannot finally decide questions such as these because there is no definite method of submitting them to experimental tests. They are closely associated with theories of the origin of the earth.

The quantities of oxygen, carbon dioxide, and nitrogen in the air are so large and the quantities added or removed by plants, animals, and chemical changes of one kind or another are relatively so small that the total quantities suffer only slight changes. Changes at one place on the earth's surface may occur to a sufficient extent to become significant, but these are soon destroyed by the winds that mix the air continuously and prevent radical departures from an average composition.

5. The Water Vapor of the Atmosphere

At a definite temperature, a liquid evaporates into a closed space above it until the pressure of the vapor attains a definite, maximum value. When this maximum vapor pressure has been attained, a state of equilibrium is said to exist between the liquid and the vapor. The space above the liquid is saturated with vapor, or the *humidity* is 100 per cent. At low temperatures, water evaporates slowly, and only a small quantity of vapor must be present in the space above the liquid to produce a humidity of 100 per

cent As the temperature rises, molecules escape from the surface of the liquid more and more rapidly Consequently, there must be more molecules per unit of volume in the space above the liquid in order that the number returning to the liquid may be equal to the number leaving Hence, as the temperature rises, more and more vapor is required to produce a humidity of 100 per cent

The *relative humidity of the air* is the ratio (expressed as per cent) of the quantity of water vapor present in a given volume to the quantity which must be present to saturate the same volume Since the partial pressure of the water vapor in the atmosphere is directly proportional to the relative amount of that substance (by volume) in a given sample, the relative humidity may be calculated by comparing the aqueous vapor pressure of air to the maximum vapor pressure of water at the same temperature Thus, the vapor pressure of water in equilibrium with water vapor at 20° is 17.5 mm If the partial pressure of the water vapor in the air at 20° is 8.75 mm, the relative humidity is 50 per cent

The water vapor in the atmosphere is produced by the evaporation of water from lakes, rivers, seas, oceans, and soil The air above a large body of water, such as the ocean, may become entirely, or almost, saturated Winds move this air over the surface of the ocean and finally blow it across the land If the temperature of the land is higher than that of the ocean, the air which was saturated with water vapor, when it was over the water, can absorb more moisture as it becomes warmer Hence the humidity falls to a value less than 100 per cent But if the saturated air that blows in from the sea is cooled, it will be capable of holding less moisture The excess may precipitate as rain or, if the temperature is sufficiently low, as snow

Because water molecules are lighter than molecules of oxygen and nitrogen, moist air is lighter than dry air Hence, air containing much moisture tends to rise At higher

elevations its temperature may be sufficiently reduced to cause the moisture that it contains to exceed the amount required for saturation If this happens, precipitation may occur The dust particles in the atmosphere play an important part in precipitation In the absence of dust, the saturation point may be exceeded without any precipitation, and the air is then said to be supersaturated with water vapor In dust-free air containing only water vapor and other gaseous constituents, the condensation of water vapor is very slow and difficult The particles of dust appear to act as nuclei about which water condenses If there are no such nuclei, the quantity of vapor per unit of volume must be several times greater than the quantity required for saturation, before precipitation begins In the absence of dust, atoms or molecules carrying electrical charges (these are called *ions*) may act as nuclei for condensation

Dew is water that condenses from the water vapor in the air upon objects on the earth's surface During the night these objects lose heat by radiation, and then temperature falls below that of the air The air which comes into direct contact with these objects is also cooled, and if cooling extends to a temperature at which the water vapor in the air exceeds the saturation point, condensation occurs Since the cooling occurs only very near the objects with which the air is in contact, water forms on these surfaces Clouds are composed of tiny droplets of water or of ice crystals, and are formed at a height where moist warm air in rising is cooled sufficiently to produce condensation and, sometimes, even freezing If the water droplets become heavy enough, they fall as drops of rain Fog is of the same character and may be thought of as a cloud very near the earth's surface

6 Ventilation

Adequate and efficient ventilating systems are essential in every building designed for work or habitation Ventilation does not

mean merely the renewal of the air supply as oxygen is removed and carbon dioxide is added by the respiration of the occupants of a room or of a building. It was once thought that discomfort and depression in closed and poorly ventilated rooms were the effects of the small percentage of oxygen and of the poisonous effects of the accumulated carbon dioxide. This belief has been disproved. Experience shows that the normal oxygen content may be decreased even as much as 50 per cent and the carbon dioxide content may become as great as three per cent (instead of the normal 0.03 per cent) without any feeling of discomfort and with complete safety to the persons who breathe the air. This does not mean, however, that such air is just as good to breathe as the normal "out-of-doors" air with its 21 per cent of oxygen and 0.03 per cent of carbon dioxide. Certainly the normal air is more invigorating, and only when we breathe it instead of air of abnormal composition may we expect normal functioning of the various parts of our bodies in which oxygen is removed from the air and is consumed. The body is accustomed to functioning under certain conditions which are represented by the average composition of the atmosphere. Naturally, it cannot be expected to adjust itself quickly to compensate for radical changes in the environment.

In a room in which the circulation of air is very poor, the carbon dioxide content may become sufficiently high to cause trouble, provided that several persons are present to manufacture and liberate this substance, but this is not a likely happening. Nor is there any experimental evidence to indicate that organic poisons—"crowd poisons"—are expelled from the lungs during respiration. The best available information on the subject indicates that the condition of the air, in a house or any other building, which determines the comfort and health of the occupants depends upon three factors: humidity, temperature, and circulation. The humidity is important because it

controls the evaporation of moisture from the skin. In closed rooms the humidity may become very high because of the water exhaled from the lungs of the occupants and evaporated from their bodies. As the humidity becomes higher and approaches the saturation point, evaporation from the skin occurs more and more slowly, and discomfort results. The same effect is noticed in summer when the humidity of the air is high. Physical discomfort results because the temperature of the body cannot be controlled by variations in the amount of moisture evaporated from the surface. Conditions may be improved by maintaining a low temperature (68° F. if possible) and by keeping the air in motion. If the air is moving, there is no opportunity for the portions immediately surrounding the body to become saturated, thus slowing down evaporation still more.

In winter, cold air containing only small quantities of moisture is brought into the rooms of houses, offices, and public build-



Courtesy of National Institute of Health

Figure 164 Laboratory Technician Working With Dangerous Materials

Her work is carried on in an isolated glass cubicle which is completely air conditioned

ings, where it is heated to a temperature of about 70° F. At this relatively high temperature, it is capable of absorbing much more moisture than it could possibly contain out-of-doors. Moisture evaporates too rapidly from the skin under these conditions, and the body is chilled. In order to remedy the situation more fuel is burned to raise the temperature of the air, but this only aggravates the situation by causing even more moisture to evaporate. In winter, therefore, provisions should be made to increase the humidity of the air. If this is not done, the skin becomes dry and cracks. Excessively dry air also causes furniture and walls to crack. Modern processes of air conditioning are now often installed in hotels, public buildings, homes, stores, and in railway trains. These processes provide for regulation of temperature, humidity, and circulation, as well as frequent renewal. For the greatest degree of comfort the air of buildings should have a relative humidity of 35 to 50 per cent in winter, and 20 to 30 per cent in summer.

THE ANALYSIS OF AIR

7 Determination of Oxygen

The percentage of oxygen in the air can be determined by exposing some substance which combines readily with oxygen to a definite volume of air. After allowing sufficient time for the reaction to be completed, the decrease in volume is measured to determine the percentage (by volume) of oxygen. Phosphorus is sometimes used to react with the oxygen. Copper is also used. A definite volume of air may be mixed with a measured volume of hydrogen and the mixture exploded by an electric spark. If the water vapor which is produced is condensed, one third of the contraction in the volume may be taken as the volume occupied by the oxygen in the sample. This calculation is based upon the combining proportion (by volume) of hydrogen and oxygen (2:1). Still another method consists in shaking a sample of air with a mixture of potassium hydroxide and pyrogallol. This mixture removes the oxygen, and the percentage

of the element is determined by measuring the contraction in volume as in other methods.

8 Determination of Water Vapor

The percentage of water vapor in the air can be determined by passing a definite volume of air through a previously weighed tube containing calcium chloride, or some other substance which combines readily with water. After the passage of the air the tube is weighed again to determine the weight of water which has been absorbed. This weight can be used to calculate the percentage of water vapor (by volume) if desired.

9 Determination of Carbon Dioxide

The percentage of carbon dioxide can be determined by passing a definite volume of air through a tube containing some substance which reacts with the dioxide. The absorbent usually employed for this purpose is sodium or potassium hydroxide, and sodium or potassium carbonate is formed. From the gain in weight of the tube containing the absorbent, the percentage of carbon dioxide by weight and by volume can be calculated.

10 Determination of Nitrogen and Argon

After the removal of oxygen, carbon dioxide, and water vapor, by the methods previously described, the residue consists chiefly of nitrogen and argon. These two gases may be separated by passing the mixture over hot magnesium. The nitrogen combines with the metal to form the nitride Mg_3N_2 , and the argon remains free. The percentage of argon is about 0.9 and that of nitrogen is approximately 78.

11 The Liquefaction of Air

The production of liquid air has become an important industry, or rather an important part of several industries which use oxygen, nitrogen, argon, and neon. In scientific work, liquid air finds considerable use whenever extremely low temperatures are desirable. It is also used to remove moisture from gases by freezing. Charcoal cooled by liquid air is used to remove gases and to produce high vacua. Mixed with finely divided charcoal or other carbona-

aceous material and packed in cartridges, it forms a powerful explosive

Because its components boil at very low temperatures (-195° to -183°), liquid air cannot be kept in an ordinary container, such as a beaker or a bottle. If it is to be preserved for any length of time, provisions must be made to insulate it from external sources of heat. This can be done by placing it in vessels so constructed that heat from the outside is conducted very slowly to the liquid air in the container. The Dewar flask, an excellent container for liquid air, is made of double glass walls, and the space between the walls is highly evacuated. Heat does not readily pass through a vacuum, hence the contents of the flask are protected from thermal conductivity. The flask is stoppered by means of a plug of loose cotton, which is also a poor conductor. The walls of the flask — in the evacuated space — may be silvered so that heat from the outside is reflected instead of being absorbed. Thermos bottles are designed in a similar manner and are used to keep liquids hot or cold by preventing heat exchanges with the surroundings.

Liquid air, like the usual state of the atmosphere, is a mixture and, therefore, has no definite melting point, boiling point, or composition. It resembles water in appearance, but it has a slightly more bluish color, which becomes more intense as the nitrogen escapes and the concentration of oxygen increases. Other properties, such as the density (average about 0.9) and the boiling point, vary with the composition. The most spectacular property of liquid air is its effect upon many common objects, an effect produced by the extremely low temperature of the substance. Flowers, vegetables, and fruits immersed in liquid air become so hard and brittle that they can be pulverized or shattered. Rubber, similarly cooled, becomes as brittle as glass. Mercury can be frozen into a hard mass, which can be used as a hammer. Substances cooled to the temperature of liquid air react very slowly, although the rate of oxidation is increased because of the effect of the greater concentration of oxygen in the liquid.

THE INERT GASES

The air contains almost one per cent, by volume, of argon and much smaller amounts of helium, neon, krypton, and xenon. Because of their chemical inactivity, these elements are called the inert gases. No compounds of these elements have ever been made, with the possible exception of a few unstable substances, such as hydrates of three of the elements and a chloride of krypton. Radon (page 247) is also an inert gas.

The inertness of these elements is explained by the structures of their atoms. For every element of the family the outermost electron group of the atom contains eight electrons, a number which we have referred to as representing the greatest possible degree of stability for the outermost group. As a result, the atoms of these elements do not lose, gain, or share electrons, and their structures represent the stability which other atoms attempt to attain in their reactions. Many of the physical properties of the inert gases are also undoubtedly related to the structure of their atoms. Not only do they fail to combine with other elements, but their atoms do not combine with each other — their molecules are monatomic. There is also very little attraction between their molecules, and cohesion is consequently very slight. Because of this condition, the velocity of the molecules must be reduced to a very low value before molecular attraction is made to prevail and the gases can be liquefied. The separation of the molecules against this weak molecular attraction is also performed without difficulty; consequently the molecules, when once reduced to the liquid state, need not be raised to a very high temperature to cause their escape. This condition results in extremely low boiling points. The densities of the gases vary considerably — from helium, which is the lightest of all gases after hydrogen, to xenon, which is about four times as heavy as air.

The boiling points and densities (under

standard conditions) of the members of this group of gases are given below

	Density g per liter	Boiling Point C° (1 atmos)
He	0.1785	-268.9
Ne	0.900	-245.9
Ar	1.782	-185.8
Kr	3.708	-151.8
Xe	5.85	-109.1

12. History of the Inert Gases

Cavendish, in 1785, was the first investigator to find evidence of the presence of the inert gases in the atmosphere — or anywhere. However, he did not realize the significance of his discovery. After causing all the nitrogen in a definite sample of air to combine with oxygen, under the influence of an electric spark, and after removing the excess of oxygen and the products of the reaction (NO and NO₂), Cavendish found that a small part (about 0.008) of the original sample of air remained. This did not appear to be nitrogen, since it could not be made to combine with oxygen; and it was not oxygen or any product of the reaction between the two elements because it was not removed by substances which effectively absorbed or reacted with these substances.

The findings of Cavendish went without explanation and with only casual consideration for more than one hundred years. In 1894, Lord Rayleigh found evidence of another sort to indicate that the atmosphere contained small quantities of one or more hitherto unknown substances. He found that the nitrogen prepared from air had slightly different properties from that prepared from some nitrogen compound, such as ammonium nitrate. In particular, he called attention to the difference in density between nitrogen samples prepared from the two sources. The sample prepared from air was always heavier than an equal volume of the other. In seeking an explanation of this difference, Lord Rayleigh was joined by Sir William Ramsay, who found a small percentage of the nitrogen-fraction of air

that would not combine with magnesium to form a nitride. It became necessary, therefore, to recognize this residue as a new element. This element was named *argon* (lazy) because of its chemical inertness. In the same year, 1894, spectroscopic evidence (page 233) led to the discovery of the element in the sun's atmosphere.

Janssen, in 1868, found a line in the spectrum of the sun which could not be identified as belonging to the spectra of any of the elements then known. Lockyer assumed that the line belonged in the spectrum of an element not known on the earth. Since the element was part of the sun, he gave it the name *helium* (sun). This element was not discovered on the earth until 1889, and was not really recognized until 1894 (by Ramsay). Discovery was made by spectroscopic examination of samples of the gas expelled when uranium-bearing minerals are heated. The spectroscope revealed the same line in the spectrum of this gas as had been observed twenty-seven years previously in the sun's spectrum.

Neon, *krypton*, and *xenon* were discovered by Ramsay and Travers in 1898. Liquid air was carefully distilled, and different fractions were collected at various temperatures. Each of the first fractions was further separated by distillation, and the different samples were studied with the aid of the spectroscope. The spectra revealed lines belonging to three hitherto unknown elements, which were called neon (new), krypton (hidden), and xenon (stranger).

Radon, previously called *niton*, is also a member of the family of inert gases. It is produced by the radioactive disintegration of radium and is itself radioactive (page 247). Because of its rapid rate of decay (page 250), this gas can never be present anywhere in any considerable quantity and is not present in the atmosphere.

13. Production and Uses of the Inert Gases

Argon, neon, krypton, and xenon are prepared by the fractional distillation or by the

fractional liquefaction of air. Both of these methods depend upon differences in the boiling points of the components of air. Until the first World War, helium was produced by heating uranium minerals and was unobtainable in large quantities. Like krypton and xenon at the present time, it had no practical value and was known only as a laboratory "curiosity," if it was known at all. It sold — if and when a purchaser was found — for about \$2500 per cubic foot. The government now operates a plant in Texas for the recovery of helium from natural gas. This plant can supply some 25,000,000 cu ft annually, and the cost of production has been reduced to about 3/1,000,000 of the cost prior to 1918.

The natural gas from wells in certain regions in Texas contains a large percentage of nitrogen and one per cent (or slightly more) of helium. The helium is recovered by liquefying the other constituents at a temperature and pressure at which helium (b.p. -268.90) remains in the gaseous state. The problem offered many difficulties but

was solved in a remarkably short time in response to the urgent demands of the country's military forces. Observation balloons and other lighter-than-air craft had previously been inflated with hydrogen. Because of its extremely combustible character, the use of hydrogen for this purpose, especially during military operations, is very dangerous. Helium, being next to hydrogen in lightness, and consequently in lifting power, was the only gas that met the requirements of low density and non-combustibility. Its density is 0.178 (grams per liter) and it has a lifting power of about 92 per cent that of hydrogen, although it is twice as heavy.

Helium mixed with oxygen is sometimes supplied under high pressures to men who must work in caissons, in diving bells, or in diving suits at considerable depths in water. When air is used, nitrogen appears to dissolve in the blood under the high pressures at which the air is taken into the lungs. When the diver emerges he is likely to develop the condition called "bends," unless

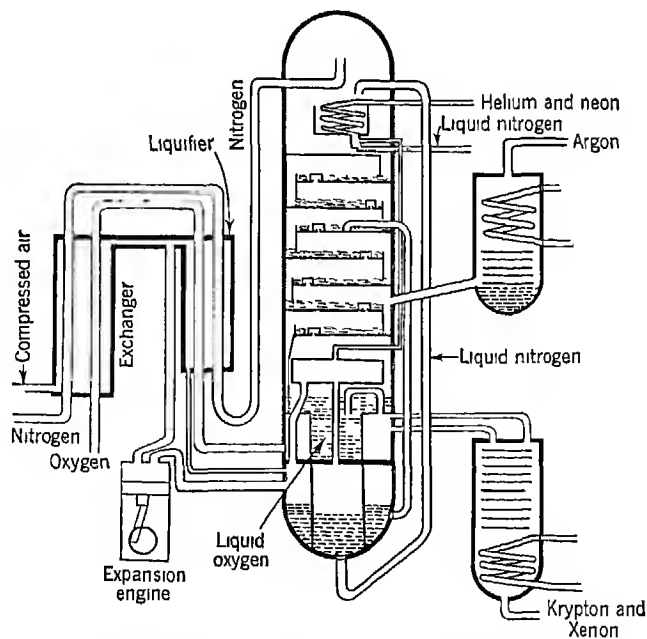


Figure 165 Diagram Showing the Parts of a Plant Designed to Separate the Different Constituents of Air

he enters a pressure-chamber, where the pressure of the air which he breathes is lowered gradually. If he steps immediately into the atmosphere, where the pressure of the air which he breathes is very much lower than that supplied him when he was beneath the surface, the nitrogen which has dissolved in his blood quickly escapes from solution and forms bubbles. This is believed to be the cause of "bends." If helium, instead of nitrogen, is used to dilute the oxygen, the danger seems to be more easily averted.

Argon is used to fill the space around the filaments in electric light bulbs. This gas does not conduct heat as well as nitrogen does, therefore, in a light bulb filled with it there is less heat lost through conduction from the filament to the glass walls and the air outside. Argon also retards the vaporization of the tungsten that composes the filament. Both of these effects allow the filament to be heated to a higher temperature and hence to emit more light.

Neon, and sometimes argon and helium, are used in producing the tubes commonly called "neon signs." These tubes are widely used as advertising signs and as beacons for ships and airplanes. They cost considerably less to operate than the old-fashioned "electric light" sign, and give better and fairer penetration, particularly through fog. The color of the light emitted by a "neon tube" depends upon the color of the glass of which the tube is made and upon the contents. Different colors are produced by different mixtures of argon, neon, and mercury vapor in tubes made of glass of various colors. The tubes are operated at about 10,000 volts but at low amperage—about 30 milliamperes (thousandths of an ampere).

Review Exercises

1. What facts show that air is a mixture and not a compound?
2. What opposing factors cause the composition of air to be almost constant?
3. Explain what is meant by the relative humid-

ity of the air. When is the humidity one hundred per cent?

4. Describe the conditions under which moisture is precipitated from the air.
5. What requirements should be met in providing adequate and efficient ventilation?
6. A sample of liquid air has a density of 0.91 and contains 24 per cent (by weight) of oxygen. What volume of oxygen under standard conditions can be produced from 10 liters of the liquid assuming that the oxygen obtained is pure and that its recovery from the liquid is complete?
7. A dry 80 ml sample of oxygen and nitrogen was mixed with 50 ml of hydrogen and the mixture exploded. After the condensation of the water vapor, the gas remaining had a volume of 100 ml and contained hydrogen and nitrogen. (a) What percentage of the original sample was oxygen? (b) What percentage of the residue was hydrogen? (Assume constant conditions.)
8. Explain the meaning of the following statement: The relative humidity of the atmosphere is 80 per cent. Is the relative humidity of the atmosphere lower generally in the winter than in the summer? Explain.
9. Why is the lifting power of helium more than 92 per cent that of hydrogen, although the density of helium is approximately twice that of hydrogen?
10. What constituents of the atmosphere are likely to vary considerably from day to day in one location?
11. Why is the air in houses during winter weather likely to be drier than in summer?
12. Describe methods used in producing the inert gases and name some of their uses.
13. Why has the spectroscope been used so extensively in the investigations of the inert gases?
14. Describe an experiment by which you could prove that the atmosphere has weight.
15. Why does the pressure at one place on the earth's surface vary?
16. How is dust related to the precipitation of moisture from the air?
17. A sample of air contained a quantity of oxygen that occupied 10 liters at a certain

temperature and under a certain pressure
What volume, measured at the same temperature and pressure, should the argon obtainable from the same sample of air occupy?

- 18 What weight and volume, under standard conditions, of carbon dioxide would have to be removed from the air to convert one ton of pure orthoclase (page 316) into the substances produced by weathering? What volume of air, approximately, contains this quantity of carbon dioxide?
19. The relative humidity of the air in a room is 30 per cent. What is the partial pressure of the water vapor in the air, if the temperature is 30° C? (See Table I, Appendix.)
- 20 Compare the amounts of water vapor in air that is saturated with vapor at 20° C and at 0° C

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THE HALOGENS

*Happy the man who, studying nature's laws,
Through known effects can trace the secret cause*

DRYDEN

1. Introduction

The first *family* of elements that we shall study consists of four members — fluorine, chlorine, bromine, and iodine — which are located in group seven of the periodic table. This family has been given the name *halogens*, which is derived from Greek words meaning “formers of sea salt” and refers to the occurrence of salts of chlorine, bromine, and iodine, and of at least traces of salts of fluorine in sea water. The most familiar of these salts is sodium chloride, NaCl, the corresponding sodium salts of the other halogens are sodium fluoride (NaF), sodium bromide (NaBr), and sodium iodide (NaI). Salts of the elements with the metals, and then hydrogen compounds, are known as the *halides*.

In discussing the properties of the halogens and their compounds, we shall emphasize family relationships. This will make our study easier to follow, and at the same time will serve to show the value and meaning of the periodic classification of the elements.

CHLORINE

2 History

Chlorine was probably first prepared in 1774 by Scheele, shortly after he had prepared oxygen. Priestley had already prepared a gas which was called, at that time, marine or muriatic acid, because it was made from “sea salt” and was known to form the solution of a strong acid when it was dissolved in water. This acid is now

called hydrogen chloride, or hydrochloric acid. Lavoisier decided that “marine-acid gas,” like all acids according to his idea of acids, contained oxygen. Scheele treated this gas with pyrolusite, or “magnesia nigra,” which is a natural form of manganese dioxide (MnO_2), and found that a rather heavy, greenish-yellow gas was produced. We now know that the product of this reaction is chlorine, but Scheele did not recognize it as an element. He called the new substance “dephlogisticated marine-acid air.” Others found that the gas would dissolve in water and that oxygen was evolved from the solution. This behavior, together with the fact that it was produced by the action of an oxidizing agent, seemed to indicate that the substance was an oxide of the same “element” as marine-acid gas itself, but that it contained more oxygen than the latter. It was called, therefore, “oxymuriatic or oxymarine acid.” This view was inconsistent with Lavoisier’s theory of acids, however, since the strength of an acid was supposed to increase with increasing oxygen content, while the green gas produced by Scheele was found to produce a weaker acid solution than the gas from which it was formed. This inconsistency with theory led Davy to attempt to produce oxygen from “oxymarine acid,” but his attempts resulted in failure. Davy decided that the substance was an element, and he gave it the name *chlorine*, because of its green color.

Davy’s discovery also made necessary a change in the conception of acids. It had already been

shown that "marine" acid can be prepared by the combination of hydrogen and chlorine. Hence, when Davy showed that chlorine is an element and contains no oxygen, it became apparent that here was one acid, at least, in which oxygen was not present. From this time on, the element common to all acids was recognized as hydrogen instead of oxygen.

3 Occurrence

Because of its pronounced activity as a non-metal and its consequent tendency to combine with metals, chlorine is never found naturally in the free state. In the combined state, however, it is one of the moderately abundant elements of the earth's crust. Its most abundant, natural compounds are the chlorides of certain metals. Of these, sodium chloride is by far the most abundant. This compound is found in sea water, which contains about 2.5 per cent of sodium chloride, in brines from salt wells, and as a mineral deposit in the earth. Rock salt is a mineral form of sodium chloride and is sometimes called "halite." Natural deposits of potassium, calcium, and magnesium chlorides are also found, usually in association with sodium chloride and such other substances as calcium sulfate and magnesium sulfate. Some of these deposits have been formed by the evaporation of sea water in arms which have been separated from the main body of the sea by geological changes in which the land was elevated. Others have been formed by the evaporation of water from lakes which have no outlets. The latter process is now going on in the Great Salt Lake and in the Dead Sea, in both of which the water contains more than 20 per cent of sodium chloride. In time, deposits formed by the evaporation of sea water may be covered by layers of sediment, several extensive deposits of this kind are known to lie below the earth's surface in many different countries. The deposits in the Stassfurt region of Germany and in Alsace-Lorraine have been mined for many years. Their value depends not upon their sodium chloride content, but upon the potassium salts

they contain. These salts, commonly called potash, are used as fertilizer.

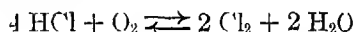
Most of the chlorides found in nature are soluble, and therefore have collected in the waters of the sea. One insoluble chloride, that of silver (AgCl), is found naturally. It is called *horn silver* and is one of the ores from which silver is obtained.

Hydrogen chloride is found naturally in the gastric juice, where as a solution of hydrochloric acid it aids in the digestion of certain kinds of foods. This acid is produced in the body in some manner from the salt contained in or added to different kinds of foods. Some animals, notably dogs, produce a larger percentage of hydrochloric acid in their gastric juice than man. In man, the normal percentage is about 0.3. Sodium chloride is also present in the blood and in various other fluids of the body.

PREPARATION OF CHLORINE BY THE OXIDATION OF HYDROGEN CHLORIDE

4 The Deacon Process

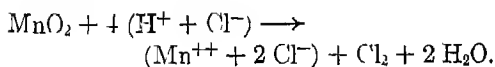
Hydrogen chloride and oxygen react very slowly at ordinary temperatures to produce chlorine and water:



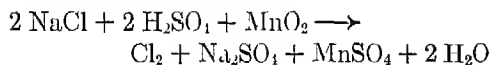
The Deacon process for producing chlorine is based upon this reaction. At one time, this process was used very extensively, but it has now been displaced, as a commercial source of chlorine, by other processes which operate at lower cost, and which also produce other substances, some of which are more valuable than the chlorine itself. In the Deacon process a mixture of hydrogen chloride and air is drawn through a chamber containing lumps of pumice that are impregnated with a solution of some copper salt, usually copper sulfate or chloride, which acts as the catalyst. The temperature at which the reaction is carried out is about 350° – 400° C. In the presence of an excess of air, about 80 per cent of the hydrogen chloride is converted into water and chlorine.

5 The Oxidation of Hydrogen Chloride by Manganese Dioxide

Chlorine is also produced by the action of many oxidizing agents upon hydrogen chloride. In preparing the element in the laboratory, pyrolusite (MnO_2) is often used. This, it will be remembered, was the reaction used by Scheele in preparing what he called "dephlogisticated marine-acid air." The manganese dioxide is placed in a flask and concentrated hydrochloric acid is added through a thistle tube or "dropping" funnel. Chlorine is evolved more rapidly if the mixture is warmed slightly. The gas is usually collected by being allowed to displace the air in an upright bottle or cylinder; it does this readily, because it is heavier than air. The reaction by which chlorine is produced is



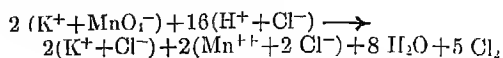
Sometimes chlorine is prepared by adding concentrated sulfuric acid to a mixture of manganese dioxide and solid sodium chloride. The reaction is the same as that between manganese dioxide and hydrogen chloride, except that sulfuric acid first acts upon the salt to liberate hydrogen chloride. (Since little or no water is present, ions are not shown in the equation.) The complete equation, omitting the intermediate steps, may be written as follows



6 The Use of Other Oxidizing Agents

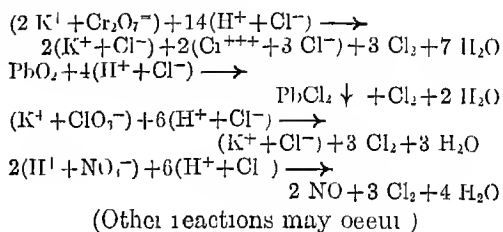
Other oxidizing agents may be used in place of manganese dioxide to liberate chlorine from hydrogen chloride or other chlorides. Potassium permanganate (KMnO_4) is sometimes used to prepare small samples of chlorine; hydrochloric acid is added to a solution of this compound, and the mixture is warmed to expel the chlorine. (Concentrated acids, especially sulfuric acid, and solid potassium permanganate liberate per-

manganic acid, which decomposes explosively, such mixtures must, therefore, *always* be avoided.) The reaction is shown by the following equation

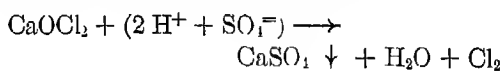


It will be noted that the valence number of manganese in this reaction is reduced from +7 to +2.

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), lead dioxide (PbO_2), potassium chlorate (KClO_3), and nitric acid (HNO_3) may also be used to oxidize hydrogen chloride. The equations for the reactions are



Chlorine is also produced by adding an acid to bleaching powder, CaOCl_2



PRODUCTION OF CHLORINE BY ELECTROLYSIS

Chlorine is usually produced, for commercial purposes, by the electrolysis of an aqueous solution of sodium chloride

7 The Cell and the Ions

The chemical changes that occur when a solution of sodium chloride is electrolyzed are explained with the help of Figure 166. The electrodes—positive *anode* and negative *cathode*—are connected to the two opposing terminals of a battery or a generator of direct current. The battery or generator produces a difference of electrical potential between the two electrodes by increasing the number of electrons on the cathode and decreasing the number on the anode (page 110). The sodium chloride, in

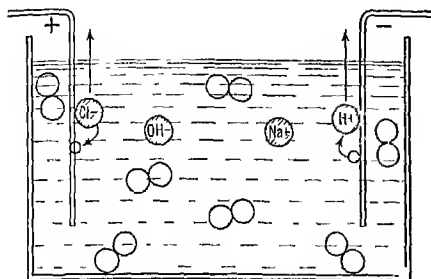


Figure 166 The Electrolysis of a Solution of Sodium Chloride

the solution of the cell, is composed of sodium and chloride ions. The properties of water indicate that it, too, contains a small number of hydrogen ions¹ and hydroxyl ions.

An aqueous solution of sodium chloride contains, therefore, molecules of water and ions of sodium, chloride, hydrogen, and hydroxyl. Under the influence of the difference of potential (voltage) existing between the anode and the cathode, the positively charged ions of sodium and hydrogen migrate, or move, toward the cathode, the negatively charged chloride and hydroxyl ions migrate toward the anode.

8 Reactions at the Cathode

Upon reaching the cathode, the positively charged sodium and hydrogen ions *may* be converted into neutral atoms. This means that an electron is transferred from the cathode to each sodium or hydrogen ion, thus restoring the number of electrons required for the electrical neutrality of the atom. Now the atoms of different metals and hydrogen show different degrees of activity in losing electrons and becoming positive ions. Sodium is more active than hydrogen, its atoms are more readily converted into positive ions than those of hydrogen. If we look at the matter from the other direc-

¹ We shall speak of these as simple hydrogen ions, H^+ , although as previously explained they are actually hydrated hydrogen ions, such as H_3O^+ . See page 155. These ions are probably produced by a reaction involving two molecules of water:



tion — starting with ions instead of atoms — the positive ions of the more active metallic elements show less tendency to acquire electrons from the cathode than the ions of the less active elements, sodium ions are converted into neutral atoms less readily than hydrogen ions. Certain voltages are required for each of these changes, and the required voltage is greater for the discharge of sodium ions than for hydrogen. This means that if the sodium ion removes an electron from the cathode, thus becoming a neutral atom, there must be a greater concentration of electrons on the cathode than is required before the hydrogen ion can remove an electron. In other words, the electrons on the cathode must be more “crowded” before the sodium ion with its relatively weak attraction for electrons can pull one away.

Hydrogen, therefore, is liberated at the cathode when the voltage is not sufficient to liberate sodium. Furthermore, if metallic sodium were liberated, it would react immediately with water to form sodium hydroxide and hydrogen. In any event, hydrogen is discharged and sodium ions remain in the solution. As hydrogen ions are discharged and removed from the solution, more molecules of water form ions. These changes lead to a greater and greater concentration of hydroxyl ions in the vicinity of the cathode. These ions and those of sodium, which remain undischarged, give a solution of sodium hydroxide. If this solution is removed from the cell and evaporated to dryness, solid sodium hydroxide is produced. This process is one of the important commercial methods by which this substance is made.

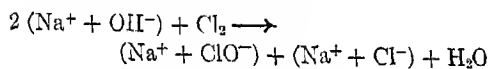
9 Reactions at the Anode

Chloride and hydroxyl ions migrate toward the anode, where the chloride ions are discharged by the transfer of an electron from each ion to the anode. This transfer leaves the chlorine atom with its normal number of seven electrons in the valence

level, and two atoms then combine with each to form the molecule, Cl_2 . Since chlorine is not very soluble in the solution, most of it escapes. The hydroxyl ion is not discharged at the anode at the voltage required to discharge the chloride ion, it is more difficult (requires a higher voltage) to remove the extra electron, which is responsible for the negative charge, from the hydroxyl ion than it is to remove this electron from the chloride ion.

10 A Commercial Type of Cell for the Production of Chlorine

The chlorine, which is discharged in the vicinity of the anode, dissolves to some extent and reacts readily with the sodium hydroxide which is present in the solution to form sodium hypochlorite (NaClO) and salt.



This reaction interferes with the production of both chlorine and sodium hydroxide and must be prevented, as far as is possible, by providing conditions which will keep the two substances separated. This is usually accomplished by separating the anode and cathode compartments of the electrolytic cell by a porous diaphragm or partition. This partition must permit the migration of the ions. Difficulty is encountered in finding a diaphragm which will effectively separate the chlorine and sodium hydroxide without offering too great a resistance to the migration of ions through the solution. The construction of a cell in which such a diaphragm is used is shown in Figure 167. Cells of this and similar design are used commercially in the production of chlorine and sodium hydroxide.

The Nelson cell consists of inner and outer compartments (Figure 167). The anode is made of graphite and is suspended from its support in the roof of the slate box in the inner compartment. The U-shaped steel plate which forms the walls of the inner compartment acts as the cathode. This is perforated and is covered on the inside with an asbestos diaphragm. A solution of sodium chloride (brine) is fed into the space inside the cathode shell. During electrolysis, chlorine is liberated at the anode and escapes through the outlet tube in the slate box. (The

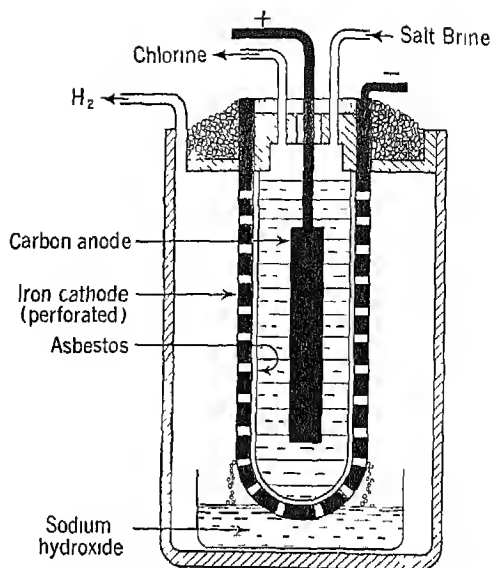
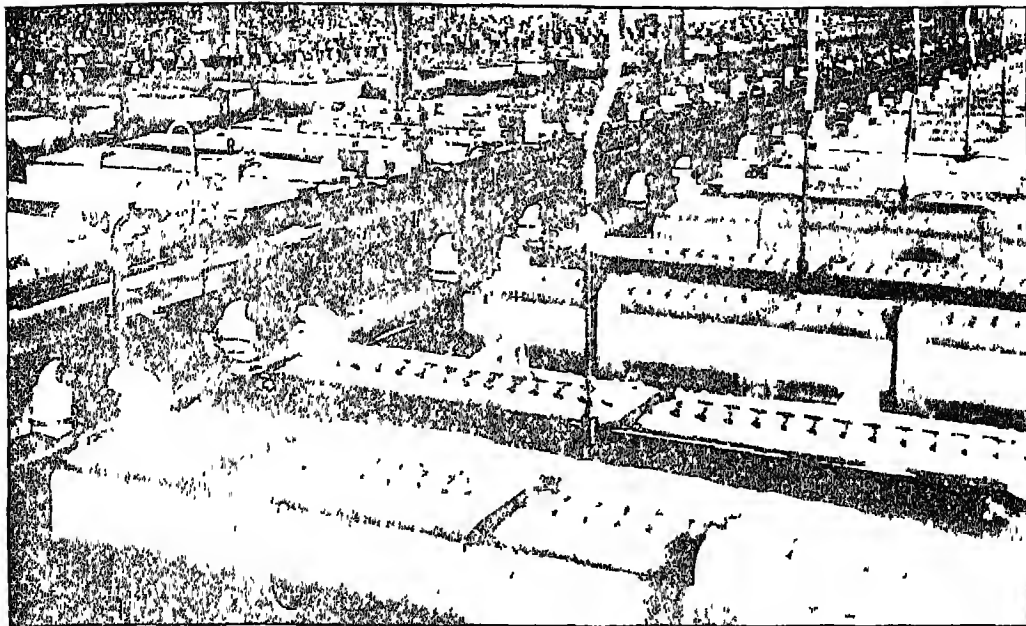


Figure 167 Diagram Showing the Cross-Section of the Nelson Electrolytic Cell

anode is made of graphite, and the box of slate, because chlorine does not attack these materials.) The sodium chloride solution seeps through the asbestos lining of the cathode and comes into contact with the perforated steel plate. Here, hydrogen is discharged and escapes from the outer compartment through an outlet tube in the top of the tank. Some sodium hydroxide is also produced in the solution which has passed through the diaphragm. This passes through the perforations in the cathode and flows down the walls of the inner compartment. The solution, which contains both sodium hydroxide and sodium chloride, collects in the receiver. This solution contains from 10 to 12 per cent of sodium hydroxide, which is separated from the salt by evaporation. The latter is less soluble than the former, and consequently is removed to a greater extent as crystals when the solution is partially evaporated.

A large cell of the type described above may consist of a long cathode vessel in which 10 to 14 graphite anodes are placed, with an asbestos lining between the anodes and the wall of the vessel. In some cells the anodes are arranged in a circle around the wall of a cylindrical vessel. Several such cells are arranged in rows or batteries (Figure 168). Each cell of the battery feeds hydrogen and chlorine into a main pipe line through which they are led to compressors where



Courtesy of The Muthusson Alkali Works

Figure 168 Batteries of Cells Used to Produce Sodium Hydroxide, Chlorine, and Hydrogen by the Electrolysis of an Aqueous Solution of Sodium Chloride

they are stored under very high pressure in steel cylinders. Chlorine may be compressed and shipped in steel tank cars.

Chlorine is also produced by the electrolysis of fused sodium chloride, a process primarily used to produce metallic sodium.

PROPERTIES AND USES OF CHLORINE

11. Physical Properties of Chlorine

Chlorine is a gas under all ordinary conditions of temperature and pressure. It has a slightly greenish-yellow color, and a sharp, disagreeable, and irritating odor. Chlorine is only slightly soluble in water, under a pressure of one atmosphere and at a temperature of 0° , it dissolves to the extent of 1.46 g of chlorine in 100 g of water. The solution is often called "chlorine water" and possesses the color and odor of the gaseous state of the element. Chlorine gradually disappears from the solution because it escapes into the air and because it reacts with water (page 334).

From its solution, chlorine may be obtained at a temperature near 0° , as the hydrate, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$.

As this hydrate has a very high vapor pressure, it decomposes very readily. In 1823, Faraday liquefied chlorine for the first time by making use of this property of the hydrate. Some of the crystals of the hydrate were placed in one end of a sealed V tube (Figure 169), and the tube was cooled in a salt and ice bath. The outside arm of the tube containing the hydrate was warmed slightly, and the chlorine that was liberated produced sufficient pressure to liquefy itself in the cold end of the tube.

When cooled to a temperature of -34.6°C , at one atmospheric of pressure, the gas changes to a greenish-yellow liquid, which freezes at -101.6° . The critical temperature

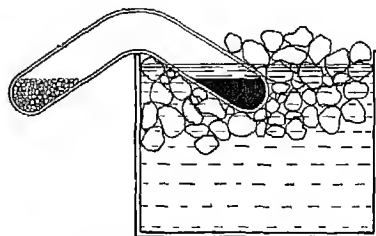


Figure 169 The Method by Which Faraday Liquefied Chlorine

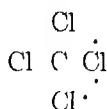
of chlorine is 144° and the critical pressure is 76.1 atmospheres. Since the weight of 22.4 standard liters of chlorine is 70.92 g, the molecular formula is Cl_2 . Its density is almost two and one-half times (exactly 2.49) that of air. The structure of an atom of chlorine is shown on page 51. The molecule consists of two atoms which share a pair of electrons



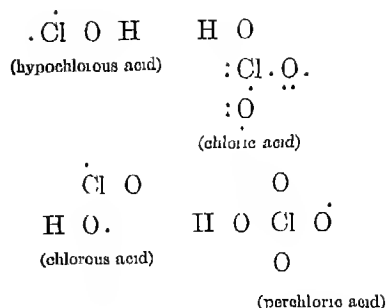
Small concentrations of chlorine in inhaled air are thought to have some value in the treatment and prevention of colds, influenza, and like disorders. In concentrations of about 0.00002 g per liter, or greater, it produces inflammation and congestion of the lungs and other parts of the respiratory system. These are the same conditions with which we are familiar in cases of very severe colds. Inhaling chlorine in large quantities is often fatal. Chlorine was used as the first poisonous gas during World War I.

12. General Chemical Properties

Chlorine is a typical non-metal. As such it resembles oxygen in some respects, but differs in showing more pronounced activity in its reactions with the metallic elements. Oxygen, on the other hand, displays a somewhat greater tendency to react with the non-metals. The most characteristic chemical activity of chlorine is its tendency to acquire a single electron per atom, thus forming the chloride ion, Cl^- . As this ion, chlorine is found in all the chlorides of the metals. It also forms covalent linkages with several kinds of atoms. In these compounds it shares one, two, three, and four pairs of electrons. Typical covalent compounds of chlorine are carbon tetrachloride,



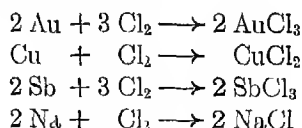
and the oxygen acids, hypochlorous, chlorous, chloric, and perchloric (page 160);



Chlorine combines directly, and often very vigorously, with most of the elements. It forms no compounds with fluorine, and although it does not combine directly with oxygen and nitrogen, very unstable compounds with these elements can be prepared by indirect methods. Three oxides of chlorine are known: the monoxide, Cl_2O , the dioxide, ClO_2 , and the heptoxide, Cl_2O_7 .

13. Reactions of Chlorine with Metals

Chlorine oxidizes all metals, and the reactions are more vigorous than with oxygen. The reaction of chlorine with gold and platinum is slow, but a thin foil of copper (if warm), or finely divided antimony (even when cold), oxidizes so rapidly that combustion results. The more active metals react very vigorously in an atmospheric chlorine. In all these reactions, chlorides of the metals are formed.



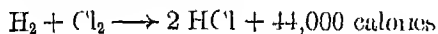
Absolutely dry chlorine does not seem to attack metals, at least, the reaction is extremely slow. Dry liquid chlorine is now shipped in tank cars in large lots or in steel cylinders in smaller quantities. The dry liquid does not corrode iron, but if moisture is present, oxidation proceeds rapidly and converts the iron into ferric chloride. The effect of moisture can be shown readily by placing a thin foil of aluminum in very carefully dried chlorine, noting the absence of a reaction, and then adding one drop of water.

14 Reaction of Chlorine with Non-Metallic Elements

Chlorine reacts with almost all of the non-metals. Carbon, nitrogen, oxygen, and fluorine are exceptions, although chlorides of the first three of these are known and can be prepared by methods other than direct combination. Phosphorus burns in an atmosphere of chlorine, forming phosphorus trichloride (PCl_3) or, in an excess of chlorine, phosphorus pentachloride (PCl_5). Chlorine reacts directly with fused sulfur to form sulfur monochloride (S_2Cl_2).

15. Reaction of Chlorine and Hydrogen

The reaction between hydrogen and chlorine is exothermic

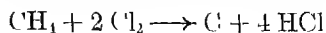


We should therefore expect these two elements to combine very readily and the product to be very stable. In the dark, however, the speed of the reaction is scarcely detectable. In ordinary light, the reaction takes place slowly. But if the mixture is exposed to direct sunlight, to ultraviolet light, or to the light produced by burning magnesium, the reaction occurs explosively. The violence of the reaction can be demonstrated by placing a flask containing a mixture of the two gases in a box made of fine wire screen and bringing a piece of burning magnesium ribbon near the container. A jet of hydrogen which is burning in the air continues to burn when introduced into an atmosphere of chlorine. Light and heat are evolved, and the reaction resembles, in every way, the reaction that occurs when hydrogen burns in oxygen, except that hydrogen chloride instead of water is produced.

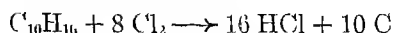
16 Reaction of Chlorine with Compounds Containing Hydrogen

Since chlorine combines very readily with free hydrogen, we should expect it also to react with compounds containing hydrogen. Natural gas, which is composed largely of methane (CH_4), continues to burn when a

lighted jet of the gas is introduced into a cylinder filled with chlorine. Hydrogen chloride and free carbon are produced

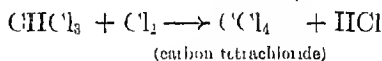
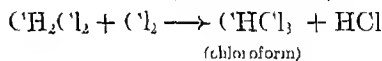
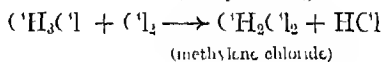
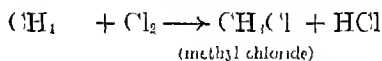


A strip of filter paper which has been wet with turpentine ignites spontaneously when lowered into a cylinder filled with chlorine. The reaction is similar to the reaction between methane and chlorine.



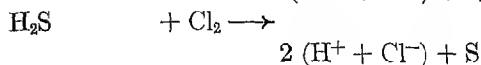
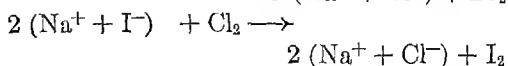
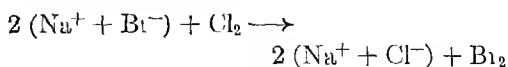
The black smoke produced in this reaction consists of particles of carbon (soot). Because of similar reactions, a lighted candle lowered into a vessel filled with chlorine continues to burn, producing a very smoky flame and a cloud of soot.

In bright sunlight a mixture of methane and chlorine reacts more slowly, and the reaction occurs in steps in which chlorine both combines with and replaces hydrogen



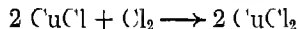
17 Reactions of Chlorine with Other Compounds

Chlorine displaces some of the non-metals from their compounds, and in doing so shows itself to be a more active non-metallic element than those which it displaces. The more common non-metals displaced by chlorine are bromine, iodine, and sulfur. Typical reactions of this kind are illustrated by the following reactions



These reactions involve the oxidation of the bromide, iodide, and sulfide by chlorine, the change involves only the transfer of electrons from the atom (or ions) of bromine, iodine, and sulfur to chlorine.

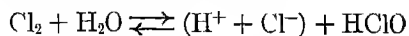
With certain compounds, chlorine combines directly to form what are sometimes called *addition compounds*. With carbon monoxide it forms phosgene, COCl_2 , one of the widely used poisonous gases of World War I. The reaction by which phosgene is produced takes place when a mixture of chlorine and carbon monoxide is passed over charcoal at 100° . When ice-cold water is saturated with chlorine, yellowish-green crystals of the hydrate, $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}$, are formed (page 331). Chlorine also reacts with compounds containing chlorine in much the same manner that oxygen reacts with certain oxides. Thus, cuprous oxide, Cu_2O , is oxidized by oxygen to cupric oxide, CuO . Similarly, cuprous chloride, CuCl , is oxidized by chlorine to cupric chloride, CuCl_2 .



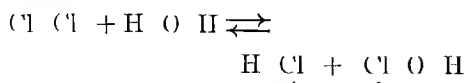
By similar reactions stannous chloride is converted to stannic chloride, SnCl_4 , mercurous chloride, Hg_2Cl_2 , to mercuric chloride, HgCl_2 , ferrous chloride, FeCl_2 , to ferric chloride, FeCl_3 , and so on. In these reactions, chlorine plays its most characteristic rôle, that of a vigorous oxidizing agent.

18 Action of Chlorine upon Water and Bases

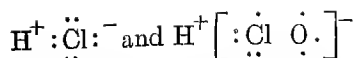
Chlorine which is dissolved in water slowly reacts with its solvent



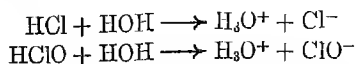
This equation may be written, also, in a manner which shows the changes in the valence electrons of the different atoms



In solution, of course, the hydrochloric acid, and also the hypochlorous acid to a smaller extent, exist as ions

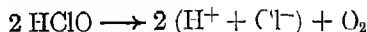


The hydrogen ion produced by these acids in the presence of water is actually the hydrated hydrogen ion, or hydronium ion, H_3O^+ . For convenience, we shall think of it here and in the discussions that follow as the simple ion, H^+ . The acids produce ions when they react with water (page 155).



Hypochlorous acid does not react to the same extent as hydrochloric acid and does not, therefore, produce as many ions.

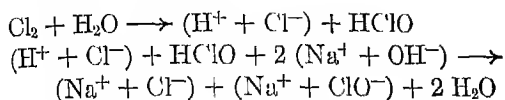
If freshly prepared "chlorine water" is used in a reaction in which chlorine itself is consumed, the reaction, which is reversible, runs almost completely to an end toward the left. But the hypochlorous acid (HClO), produced by the reaction toward the right, is unstable, especially in the light



As this acid decomposes, the reaction toward the right is completed and the chlorine disappears, hence, a solution which has stood for some time, especially if it has been exposed to the light, contains nothing but hydrochloric acid and perhaps some dissolved oxygen. The reaction may also occur toward the right in a freshly prepared solution of chlorine in water, if a substance readily oxidized by oxygen is present, the hypochlorous acid acts directly as the oxidizing agent, and chlorine acts only indirectly. This reaction is of importance in the use of chlorine for bleaching purposes, the direct bleaching agent is the oxygen which is liberated in the atomic form by hypochlorous acid. It is evident that chlorine itself does not bleach since water is necessary for the desired effects.

If a base is added, the reaction also goes to an end toward the right, since the two acids are neutralized. Thus, sodium hydroxide, when added to a solution of chlorine, forms sodium chloride and sodium

hypochlorite (NaClO) The complete equation for the reaction in the presence of sodium hydroxide is



If the solution is heated, sodium chlorate (NaClO_3) is obtained instead of the hypochlorite.

19. Tests for Chlorine

Free chlorine can be detected by employing the reaction in which it displaces iodine from an iodide. A strip of filter paper is moistened with a solution of sodium or potassium iodide which contains a suspension of starch (iodostarch paper). When this paper is brought into contact with free chlorine, iodine is liberated and produces a dark blue coloration of the starch. Since iodine is also liberated by other substances, including bromine and ozone, this is not a specific test for chlorine. Other substances which produce the same effect must be eliminated, or shown to be absent, before this reaction is used to detect chlorine.

Combined chlorine, if it is present in solution as a chloride of a metal or as hydrochloric acid, is detected by adding a solution of silver nitrate. The chloride ion is precipitated as silver chloride, AgCl , which forms a white, curd-like precipitate. This substance darkens upon exposure to the light due to decomposition, which liberates free silver. Concentrated nitric acid is added in making this test to dissolve other salts of silver. Here again, however, certain other ions which form silver salts that are not soluble in nitric acid must be absent, or if present must be removed, before this test can be relied upon. The test may be confirmed by adding ammonium hydroxide to the precipitate. Silver chloride dissolves. If the mixture is then filtered, the addition of nitric acid to the filtrate causes silver chloride to form once more.

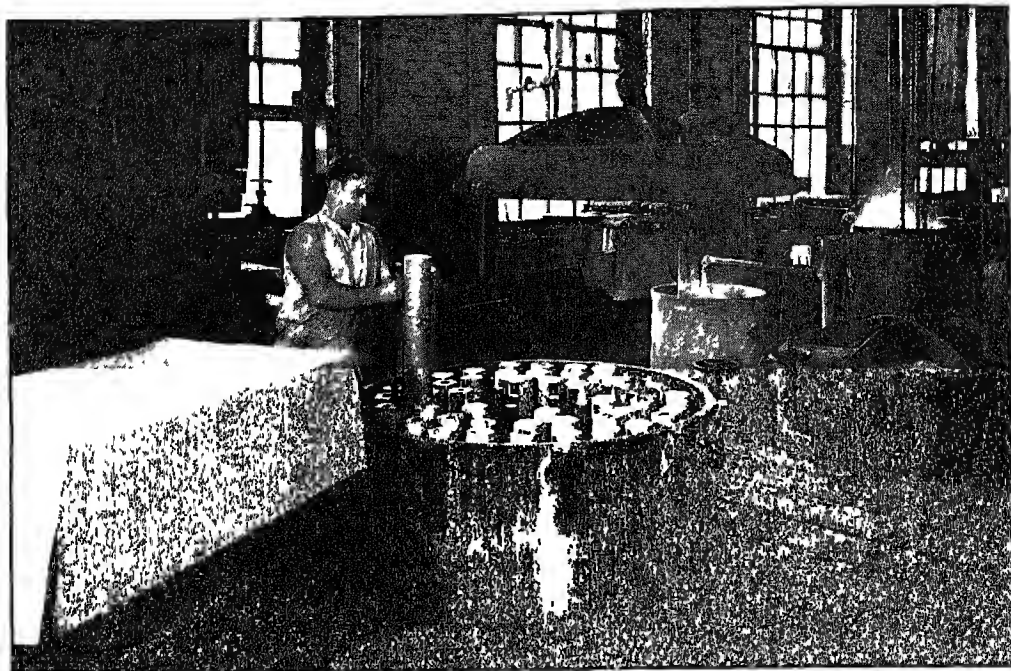
20. Uses of Chlorine

(a) The use of chlorine which consumes the largest quantities of the element is

bleaching. It is used as a bleaching agent in the textile industry and in the preparation of materials, such as wood pulp, from which paper is made. Certain textiles, such as wool and silk, which are made from animal fibers, cannot be bleached by chlorine because they are attacked too easily and are seriously damaged. Cotton cloth is not attacked so readily, but even this variety of fabric must be washed thoroughly to remove the excess of chlorine and hypochlorous acid. As a washing fluid, a solution of sodium thiosulfate, which converts the chlorine and hypochlorite into sodium chloride, is used instead of pure water. As already explained (page 334), the bleaching action of chlorine is due directly to oxidation by hypochlorous acid. Water is therefore necessary in the process. Bleaching is a process in which the colored compounds found in natural fibers, as well as most synthetic coloring substances (dyes), are converted by the oxygen which hypochlorous acid liberates into colorless compounds. Instead of free chlorine, bleaching powder, CaOCl_2 , and substances containing the hypochlorite ion, ClO^- , e. g., sodium hypochlorite, NaClO , are generally used as bleaching agents.

(b) Chlorine is used to purify water for drinking purposes and for use in swimming pools. Liquid chlorine in steel cylinders is supplied for this purpose. All dangerous microorganisms can be destroyed by as little as 0.3 to 1.5 parts of chlorine in 1,000,000 parts of water, although an excess, which may be removed later, is sometimes added (page 334). The part that has been played by chlorine in overcoming epidemics of diseases, such as typhoid and dysentery, is one of the most noteworthy contributions of modern sanitation to man's well-being.

(c) Chlorine is used in the preparation of germicidal solutions which contain, usually, sodium hypochlorite. One of the best known of these — Dakin's solution — is made by treating a solution of sodium carbonate (Na_2CO_3) with chlorine. The product is a solution containing sodium hypochlorite



Courtesy of Philadelphia Quartz Company

Figure 170. Bleaching Room
Showing the large kiers or vats in which materials are bleached

and sodium chloride. This antiseptic was used extensively during World War I in the treatment of wounds. By preventing infection, it undoubtedly saved many lives. A solution containing the same substances is sold as a household antiseptic under different trade names. It is one of the more effective antiseptics.

(d) Chlorine is used in the manufacture of many dyes, drugs, explosives, disinfectants, and the chlorides of sulfur, arsenic, aluminum, tin, antimony, carbon, silicon, and phosphorus.

(e) Gold may be extracted from its ores by causing chlorine to react with the metal to form auric chloride, AuCl_3 . Tin may be recovered from "tin" cans by treating them with chlorine, which converts the coating of tin on the surface of the iron sheet into stannic chloride, SnCl_4 .

(f) Chlorine is used in the manufacture of bleaching powder, CaOCl_2 . This product formerly had wide usage in the purification

of water, a use for which liquid chlorine is employed today.

(g) Chlorine was used as the first poisonous gas during World War I. It was distributed in tanks along the front line trenches, and was released when the direction in which the wind was blowing was favorable for carrying the dense clouds of the gas in the enemy's direction. It was later placed in shells by means of which the gas was scattered within enemy territory. Before the end of the war, gases which were more poisonous largely replaced chlorine. For the most part these were liquid chlorine compounds, which volatilized readily when shells containing them burst. Two of the most extensively used poisonous substances were phosgene, COCl_2 , and mustard gas, $(\text{C}_2\text{H}_4)_2\text{Cl}_2\text{S}$, which is called in chemistry dichlorodiethyl sulfide. "Tear" and "sneeze" gases also often contain chlorine. Chloropicrin, CCl_3NO_2 , is a "tear gas," and diphenylchloroarsine, $(\text{C}_6\text{H}_5)_2\text{AsCl}$, is a "sneeze gas."

BROMINE

21 History

The credit for the discovery of bromine is usually given to Balard, who first recognized the substance as an element in 1826, although Liebig is said to have first produced the free element sometime prior to that date. Liebig believed, however, that the substance he produced was a compound of chlorine and iodine. The liquid remaining when salt is recovered by crystallization from sea water, or from salt brines, contains bromide, iodide, and several metallic ions. Balard and Liebig produced bromine by treating this "mother liquor" with chlorine and also by treating the residue from the evaporation of this liquor with manganese dioxide and concentrated sulfuric acid. Iodine was also liberated in both of these processes. Balard observed that two different substances were produced and successfully separated them by distilling the bromine from the mixture. He showed that the product was a new element for which the name bromine, meaning *stench*, was suggested. The element was prepared by others, but they, like Liebig, mistakenly called it a chloride of iodine.

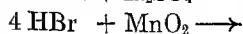
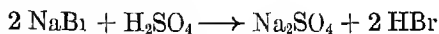
22. Occurrence

Bromine is not found naturally in the free state. It occurs usually as sodium, potassium, or magnesium bromide, along with sodium chloride in salt deposits, such as the famous Stassfurt beds, in sea water, in the brines from salt wells, and in the waters of the Dead Sea and the Great Salt Lake. When sea water, or a more concentrated solution of sodium chloride from salt wells, is evaporated, the chlorides are less soluble and are therefore deposited first. The bromides tend to collect in the "mother liquor," from which bromine is removed by methods similar to those used by Balard in discovering the element.

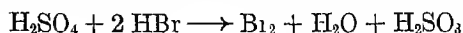
23 Laboratory Production

The methods used to produce chlorine by

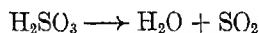
the oxidation of its compounds can also be used to produce bromine. For example, bromine is liberated by the action of manganese dioxide and sulfuric acid upon solid sodium bromide.



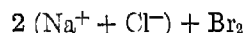
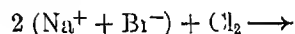
Even concentrated sulfuric acid, itself, oxidizes the bromine in hydrogen bromide.



The sulfurous acid is unstable and decomposes in a manner similar to carbonic acid (page 301).



Bromine is also liberated from bromides by the action of chlorine as an oxidizing agent.

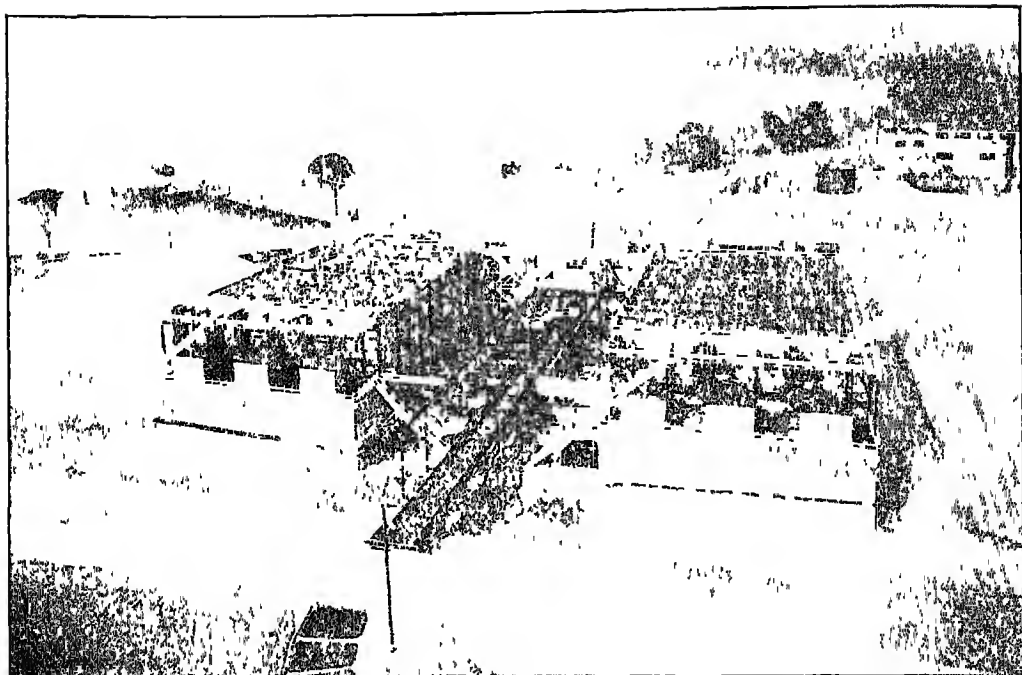


The bromine produced by any of these reactions is purified by distillation. Since it is liquid under ordinary conditions, bromine can be collected in a receiver that is cooled by immersion in cold water.

24 The Production of Bromine for Commercial Uses

Until about 1934, most of the bromine produced in this country was recovered from brines pumped from salt wells in Michigan and a few places in the Ohio Valley. In recent years, sea water has become an important source of supply. The concentration of bromide ion in the water of the oceans is very small — about 67 parts per million — but the total quantity in the water of all the oceans can be measured in billions of tons.

The location of a plant for the extraction of bromine from sea water is very important. Preferably, it should be located on an arm of land that extends for some distance into the ocean,



Courtesy of The Dow Chemical Company

Figure 171 Bromine Extraction Plant

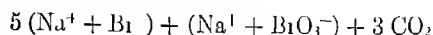
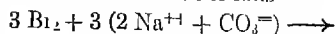
This plant is located near Wilmington, North Carolina. Bromine is extracted from sea water. The flume through which sea water passes into the plant is shown in the foreground.

so that ocean water can be withdrawn for use on one side and the water, after use, can be discharged on the other. In this manner, the water to be used is not allowed to mix with water from which the bromine has been removed. The plant should not be located near the mouth of a river, the water from which dilutes the water of the ocean. Transportation facilities and the materials necessary for the operation of the plant — salt from which to make chlorine, for example — should be readily available. The climate should be warm during most of the year, because the water must be warmer than it is as it comes from the ocean for the maximum efficiency of the process; the sun's heat provides an inexpensive method of raising the temperature of the water after it has been pumped from the sea into shallow basins.

A desirable location was found at Wilmington, North Carolina, and there, in 1934, the first plant for the extraction of bromine from the sea was built. Water is pumped from the ocean on the north side of a peninsula, and after the

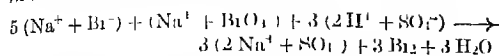
bromine has been extracted, the waste water is discharged into a river that carries it to the sea at a point far removed from the plant. The water is first pumped into ponds, where it is heated by the sun until its temperature has risen several degrees.

When ready to be treated for the extraction of bromine, the water is acidified slightly with sulfuric acid; the bromine is then liberated in a tower into which the water is sprayed and through which chlorine is passed. The bromine is removed from the water that collects at the base of the tower by an air into which the bromine vaporizes (page 205). The air with its load of bromine vapor is then passed into a second tower, where it comes into contact with a solution of sodium carbonate that flows from the top of the tower over tile or stone. Here the bromine reacts to form bromide and bromate ions.

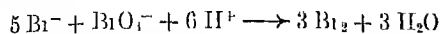


The mixture of sodium bromide and sodium

bromate is then treated with sulfuric acid, and bromine is liberated



This reaction may also be written in the following form, which shows only the ions actually involved



The plant at Wilmington has a capacity production of about 25 tons of bromine per day. The extraction from Michigan brines is based upon the same reactions.

25. Physical Properties

Under ordinary conditions bromine is a dark reddish-brown liquid, which evolves a dense brown vapor. Its boiling point is 59°C , as compared with -34.5° for chlorine. Its freezing point is -7.3° as compared with -102° for chlorine. Its density at 0° (weight of 1 ml) is about 3.12. Its solubility in water at 0° and 760 mm is about 4.22 g. per 100 g. of water. It is therefore considerably more soluble than chlorine under the same conditions. The aqueous solution is called "bromine water." Bromine dissolves much more readily in certain organic liquids than it does in water. Carbon disulfide, carbon tetrachloride, ether, and chloroform dissolve it readily, forming solutions which vary in color from straw to dark reddish-brown, depending upon the concentration of the bromine.

Bromine has a very disagreeable odor. It irritates the eyes and, when breathed, produces serious inflammation of the respiratory tract. When the liquid is spilled on the flesh it produces serious burns, which are extremely slow in healing. Bromine is one of the elements that must be handled at all times with extreme caution. It is more dangerous than iodine because it is a volatile liquid, and more dangerous than chlorine because the latter is seldom used in the concentrated liquid form.

26. Chemical Properties

In its chemical behavior bromine re-

sembles chlorine very closely. The difference lies only in the greater activity of chlorine. Bromine does not combine with the least active metals, such as platinum and gold, but it does form mercuric bromide (HgBr_2) with mercury. The more active metals are attacked readily. Bromine also reacts with fewer non-metals than chlorine, and its reactions are less vigorous. It does not combine directly with oxygen, carbon, chlorine, or nitrogen. It combines with phosphorus to form the tribromide and the pentabromide, and with sulfur to form the monobromide, S_2Br_2 . Bromine combines with iodine to form the bromide, IBr , and with fluorine, the fluoride, BrF_3 . In the former, iodine acts as a more positive element than bromine, and in the latter, bromine is more positive in character than fluorine. With hydrogen, bromine reacts very slowly at low temperatures but more rapidly at high temperatures, particularly in bright light or in the presence of platinum, which acts as a catalyst of the reaction. Bromine reacts with compounds containing hydrogen, such as the hydrocarbons, less vigorously than chlorine but in a similar manner. Its reaction with water also corresponds to the reaction of chlorine, but oxygen is liberated only very slowly from water by bromine. Hypobromous acid, HBrO , is first formed. Bromine is displaced from bromides by fluorine and chlorine, and, in turn, displaces iodine from iodides.

27. Uses of Bromine

The demand for bromine increased many fold about 1930. Prior to that time, the production in the United States was about 1000 tons annually. It rapidly increased to four or five times this amount in 1931-32 and is now normally about 45,000 tons. This increase was caused by the use of bromine in the production of ethylene dibromide, $\text{C}_2\text{H}_4\text{Br}_2$, which must be mixed with tetraethyl lead in producing anti-knock gasoline for motor fuel. It is also used to produce silver bromide, which is the light-sensitive

substance that is suspended in the gelatine coating of photographic films and plates. Potassium and sodium bromides are used in medicine as sedatives for the nerves and in the treatment of epilepsy and "lockjaw." Bromine itself is used to a very limited extent as a disinfectant and to a much greater extent in the manufacture of several organic compounds, among which are certain important dyes. It is also used to manufacture "tear" gases, of which bromo-acetone is an example.

IODINE

28 History

Because of our acquaintance with "tincture" of iodine as a household antiseptic, most of us are more familiar with iodine than with the rest of the halogens. This "tincture" is an alcoholic solution of iodine. The element, itself, is a black-purple solid.

Iodine was first prepared shortly after Davy had demonstrated that chlorine, or "marine acid oxide," as that substance was first called, is an element. By heating the ash of certain sea weeds with concentrated sulfuric acid, Courtois prepared a substance which evolved violet vapor, but he did not recognize the substance producing these vapors as an element. We now know that the ash he used contained iodides, as well as chlorides and bromides. The iodides reacted with sulfuric acid to give hydriodic acid, HI , which, in turn, was oxidized to free iodine. The discovery that the substance prepared by Courtois is an element was made by Gay-Lussac in 1814. He named it *iodine* from the Greek word meaning *violet*.

29 Iodine in Our Bodies

Iodine is essential to our physical well-being, although each of our bodies contains, on the average, only about 50 mg of the element in the form of its compounds. A compound of iodine, called *iodothyronin*, is found in the thyroid gland of the neck. When iodine is not provided, the gland does

not function properly, and one form of goiter or, sometimes, cretinism develops. Normally, sufficient iodine is supplied as iodides in water or as iodine compounds in certain kinds of foods, such as green beans, spinach, milk, and butter. Sometimes, however, the soil contains little or no iodine in the combined state, and since this is the indirect source of the supply, whatever the direct source may be, the food we eat and the water we drink do not supply the iodine that is required by the thyroid gland. Salt, used in seasoning food, sometimes has a little sodium iodide added to it and is called "iodized" salt. Goiter is most common among the inhabitants of inland regions. Near the oceans, waters from the earth contain more chloride and also more iodide, and the average diet usually contains more sea foods, which contain iodine. Among persons whose diet contains large amounts of sea foods, goiter is almost an unknown disease.

30 Occurrence

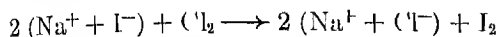
Iodides occur with bromides in the solution remaining after sodium chloride is crystallized from sea water and from the brines of salt wells and salt lakes. Most of the iodine produced in this country is recovered from brines obtained from wells in California. Iodine also occurs in sea weeds, and some has been extracted on a commercial scale from the giant kelp that grows along the Pacific coast of the United States.

Until recently, most of the world's supply of iodine came from the sodium nitrate beds of Chile, where it occurs as sodium iodate, NaIO_3 .

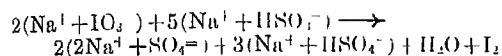
31 Preparation

The methods of producing iodine in the laboratory are similar to those used in producing bromine. In general, the iodide ion is oxidized to the free element more easily than any of the other halide ions. Thus, iodine is readily liberated from an iodide by the action of concentrated sulfuric acid,

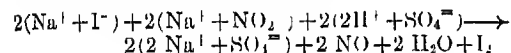
which has no oxidizing effect upon a chloride. The ashes of kelp may be treated with manganese dioxide and sulfuric acid or suspended in water and treated with chlorine. By the latter method, iodine may be liberated also from brines.



Iodine is recovered from the sodium iodate that is present in Chile saltpeter by means of sodium bisulfite, which acts as a reducing agent.



Iodine may be separated from other substances produced at the same time or added during its recovery by evaporating to dryness the solutions in which it is liberated and heating the residue, iodine sublimes (page 15). In the recovery of iodine from the brines of oil wells, a solution of sodium nitrite, NaNO_2 , containing sulfuric acid is added to liberate the iodine.



Iodine is recovered from the dilute solution that results from this reaction by being adsorbed on charcoal. It is then removed from the charcoal by means of sodium carbonate with which it forms sodium iodate and sodium iodide. Sulfuric acid is then added to produce free iodine. These reactions are very similar to those used in the recovery of bromine (page 339).

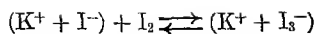
32 Properties

At ordinary temperatures, iodine forms dark or blackish-purple and slightly lustrous crystalline plates. Its melting point is 114° , its boiling point is 184° , and its density is 4.93 g per cc. When heated below the boiling point, the solid changes into violet vapor, it can therefore be sublimed. At temperatures slightly above the boiling point, the formula of the vapor appears to be I_2 , but at 700° and higher temperatures, considerable quantities are dissociated, form-

ing monatomic molecules, I . Molecules of iodine in solution also appear to have the formula I_2 , and this is true, also, for the solid state as shown by X-ray analysis of iodine crystals. Iodine dissolves in water, in ethyl alcohol, and in other solvents of high dielectric constant, to form brown-colored solutions. The solubility in water at 25°C is about 0.03 g per liter. It dissolves in much larger quantities in organic solvents of low dielectric constants, such as ether, carbon tetrachloride, benzene, and chloroform, forming violet-colored solutions.

Chemically, its behavior is much like that of the other halogens. It is the least active member of the family, reacting less vigorously than fluorine, chlorine, or bromine with hydrogen and with the metals. The oxides I_2O_4 , I_4O_9 , and I_2O_5 may be formed indirectly. It forms the fluoride, IF_5 , the bromide, IBr , and the chlorides, ICl and ICl_3 , in all of which it acts as the more positive element. Iodine reacts with phosphorus to form the iodides, P_2I_4 and PI_3 , but does not form the pentaiodide, PI_5 . With hydrogen, iodine reacts very slowly and incompletely at ordinary temperatures, but more rapidly at higher temperatures, in bright light, and in the presence of catalysts to form hydrogen iodide, HI . It combines with all the active and with some of the inactive metals, such as mercury. Mercuric iodide can be formed by grinding mercury and iodine together in a mortar. Iodine is displaced from iodides by all the other halogens and can be displaced from its combination with hydrogen (HI) by oxygen. It is therefore a less vigorous oxidizing agent than oxygen or any of the members of its own family. Iodine oxidizes metallic iron to ferrous ion only, whereas bromine and chlorine each form ferric ion. Iodine shows much less tendency than chlorine or even bromine to substitute for hydrogen in hydrocarbons.

Solutions containing the iodide ion dissolve much more iodine than will dissolve in the pure solvent. This is due to the formation of the triiodide complex ion.



The reversibility of this reaction makes possible an aqueous solution containing much more available iodine (for reactions with other substances) than is possible when iodine is dissolved alone in water. The solubilities of chlorine and bromine are also increased by the presence of chloride and bromide ions. It appears likely that a molecule of any halogen may act as the iodine molecule reacts, as shown in the equation above, and that some compounds of the character of $KBrCl_2$ may be possible.

33 Uses

Iodine's best-known use is as an antiseptic. For this purpose "tincture" of iodine, which is a solution of the element in alcohol, is employed. It is one of the most efficient household antiseptics. Iodine is also used to produce iodoform, a yellow powder, which is likewise used as an antiseptic. Silver iodide is used in photography in the same manner as silver bromide. Iodine is used in the synthesis of many organic compounds, of which some of the aniline dyes are probably most important. The use of iodine in the prevention and treatment of goiter has been mentioned previously. The element is also used to produce the iodides of the metals, which are used as laboratory reagents. Of these sodium and potassium iodides are most important. The so-called "colorless iodine," which is used as an antiseptic, is a compound of iodine, usually di-iodohydroxypropane, $(C_2H_5I)_2CHOH$. A colloidal form of iodine is also used as an antiseptic.

34 Test

The usual method of detecting *free* iodine depends upon the blue color produced when iodine comes into contact with starch. The color is not caused by the formation of a blue compound, but is probably the result of the adsorption of iodine by starch. To use this test, iodine if combined must first be converted into the free element by the use of an oxidizing agent, if it is present as an iodide, and by the use of a reducing agent, if it is present in compounds such as $NaIO_3$.

FLUORINE

35 Occurrence

Fluorine is approximately one half as abundant in the earth's crust as chlorine, and about 100 times as plentiful as bromine and iodine. Because of its extreme activity, it is never found free. Its most widely distributed compound is fluorspar, CaF_2 , but it occurs also in cryolite, Na_3AlF_6 , and fluorapatite, $CaF_2 \cdot Ca_3(PO_4)_2$. Very small traces are present in sea water. It is also present in the enamel which covers the teeth. Fluorspar serves as the source of practically all fluorine compounds. It is a mineral which occurs as cubical crystals of many different colors. The crystals glow or "fluoresce" in a dark room after they have been exposed to bright sunlight, the name *fluorescence* is derived from this property of fluorspar.

36 Preparation

Hydrofluoric acid and several other compounds of fluorine were known long before the element was prepared in the free state, in 1886, by Moissan, who prepared it by electrolyzing a solution of potassium fluoride in pure hydrofluoric acid. The difficulty encountered in preparing fluorine is caused by its tendency to react with almost every substance. Moissan used an electrolytic cell (Figure 172) made in the shape of a letter

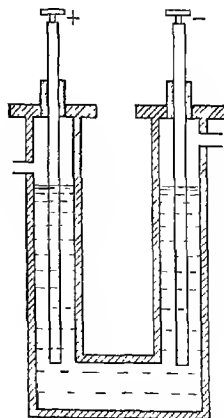


Figure 172 Electrolytic Cell for the Production of Fluorine

U, and constructed of an alloy of platinum and iridium. The electrodes were made of the same material and were suspended from fluorspar stoppers placed in the openings of the arms of the tubes. Fluorspar is a mineral containing fluorine and is therefore resistant to the action of the element. The cell was cooled to about -23°C ., during its operation, by a bath containing liquid methyl chloride, CH_3Cl . The fluorine was liberated at the anode and was collected in platinum tubes. Fluorine is now produced commercially by the electrolysis of a solution of potassium fluoride in anhydrous hydrogen fluoride in a cell similar to the one used to produce chlorine. The anodes of the cell are made of carbon and the cathodes of copper or steel. These metals are attacked by fluorine, but they are protected from extensive action by the formation of a coating of the fluoride of the metal. In some cells the vessel is made of magnesium or Monel metal and the electrodes of graphite. Fused potassium acid fluoride, KHF_2 , has also been used as the electrolyte. An aqueous solution cannot be used, because fluorine, if it is liberated, reacts immediately with water.

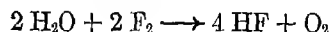
Fluorine cannot be produced by the oxidation of hydrogen fluoride as chlorine is produced from hydrogen chloride. Such a reaction is not possible in the case of fluorine because the element itself is the most vigorous oxidizing agent. There is consequently no oxidizing agent that will liberate it from a fluoride. When the fluorine atom reacts, it acquires one electron and becomes a fluoride ion, F^- , except in a few compounds in which it shares electrons, as it does, for example, in boron trifluoride, BF_3 . No other atom or ion has as much attraction for this electron as the fluoride ion has, hence the fluoride ion retains the electron that is responsible for its charge, regardless of the substance that may be brought into contact with it. The fluoride ion is oxidized to free fluorine, therefore, not by the atoms or ions of another element, but by electrolysis.

37 Properties

Fluorine is a pale greenish-yellow gas. Its molecules have the formula F_2 , and its den-

sity, therefore, is slightly greater (1.3 times) than that of air. It has a very irritating effect upon the mucous membrane and is very poisonous. It has been condensed to a liquid at -187° , its boiling point at one atmosphere; it solidifies at -223° .

Fluorine does not dissolve in water; instead, it reacts vigorously with the water, forming hydrogen fluoride and oxygen.



At the same time, a compound of fluorine and oxygen, F_2O , is also formed. Some ozone may be produced during the reaction, although this is open to question.

Fluorine reacts with more elements, and reacts more vigorously, than any other element. It combines explosively with hydrogen in the dark and at temperatures as low as -253° , although at this temperature fluorine is a solid and hydrogen is a liquid. Carbon, which does not combine directly with the other halogens, ignites spontaneously in an atmosphere of fluorine. Non-metals and metals that react with chlorine react much more vigorously with fluorine. Fluorine reacts with all the elements except nitrogen, chlorine, and the inert gases. With oxygen, however, fluorine shows less disposition to form compounds than chlorine; two oxygen compounds, F_2O and F_2O_2 , have been prepared; these are to be regarded, probably, as oxygen fluorides. Fluorine replaces all other halogens and in fact all other non-metallic elements from their compounds with hydrogen and the metals. No compounds of fluorine corresponding to the chlorites and chlorates are known, with the possible exception of the acid, HFO . Glass, asbestos, and even water undergo vigorous combustion in pure fluorine.

38 Uses

Fluorine, itself, has few uses because of the difficulties involved in producing, storing and transporting it in large quantities. Com-

pounds of fluorine have important uses. Uranium hexafluoride has been used in the vapor state (it sublimates at slightly above 50°) in the separation of the isotopes of uranium (page 283). The lighter molecules containing atoms of ^{235}U diffuse through a porous membrane more rapidly than the molecules containing ^{238}U . Certain fluorine derivatives of hydrocarbons, e.g., difluorodichloromethane, CF_2Cl_2 , in which two chlorine and two fluorine atoms replace the four atoms of hydrogen in CH_4 , are used as the fluid in domestic "electric" refrigerators.

The fluoride of calcium plays an important natural part in building up bones and the enamel of the teeth. More than a mere trace of fluoride ion (3 parts per million) in drinking water causes abnormal growth of the teeth and mottling of the enamel. Smaller amounts are thought to be beneficial in preventing dental caries (decay). Fluorides are also present, in very small traces, in the blood and have been suggested as related in some way to the tendency of blood to form clots. The mineral, fluorapatite, is used as a flux, which combines with various substances that cannot be melted readily to form easily fused substances. Ammonium fluoride is used as a disinfectant in brewery vats. Sodium fluoride is used as an insecticide, as a flux, and to treat wood so that it will not be attacked by fungi. Cryolite, Na_3AlF_6 , is used in the preparation of metallic aluminum.

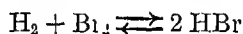
Hydrofluoric acid, or a fluoride mixed with sulfuric acid, is used to etch the graduations on thermometer stems, burettes, graduated cylinders, and other glassware. Hydrofluoric acid is also used as a laboratory reagent in certain analytical procedures which deal with the detection and estimation of the quantity of silica or silicates in rocks and other materials. The acid reacts with silica, either free or combined as silicates, to form silicon fluoride, which is a gas and consequently escapes. The quantity of silicon or silica (the oxide) can be calculated from the loss in weight.

THE HYDROGEN HALIDES

At one time great care was taken to refer to pure HF , HCl , HBr , or HI as hydrogen fluoride, chloride, bromide, or iodide and to their aqueous solutions as hydrofluoric, hydrochloric, hydrobromic, and hydriodic acids. This distinction has disappeared almost entirely with the introduction of new ideas concerning the nature of acids (page 156).

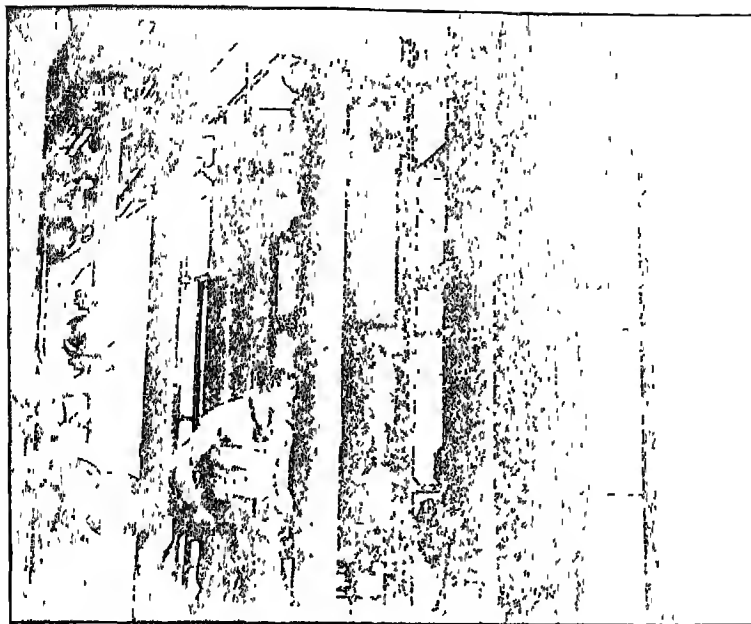
39. Preparation by Direct Combination

Compounds of hydrogen and the halogens can be prepared by the direct combination of the elements. The vigor of the reaction varies, however, from a combination with explosive violence in the case of fluorine to the reaction of hydrogen and iodine, which is very slow and incomplete regardless of conditions. Chlorine and hydrogen combine explosively when exposed to a bright light, and a jet of hydrogen burning in the air continues to burn in an atmosphere of chlorine, forming hydrogen chloride. A mixture of hydrogen and bromine, when heated, forms colorless hydrogen bromide.



This reaction is reversible and consequently pure hydrobromic acid or a concentrated solution of it is likely to have a brown or straw color because of the presence of free bromine. This result is especially likely if the substance is heated to a moderately high temperature. If a mixture of iodine vapor and hydrogen is heated to a moderately high temperature, some hydrogen iodide is formed since the reaction is reversible, especially at high temperatures, the reaction is never complete.

Considerable hydrochloric acid is now produced by the direct combination of the elements. This reaction is carried out at moderately low temperatures. A catalyst, usually charcoal, is used to increase the speed of the reaction.



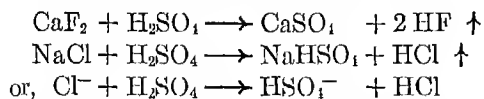
Courtesy of Hooker Electrochemical Company

Figure 173 Manufacture of Hydrochloric Acid

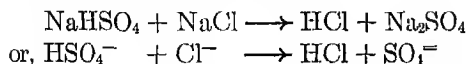
Anhydrous hydrogen chloride is synthesized from chlorine gas and hydrogen gas in these burners, one of which is being lighted by an operator

40. Production of Hydrofluoric and Hydrochloric Acids in the Laboratory

Hydrofluoric and hydrochloric acids are most often made in the laboratory by the action of concentrated sulfuric acid upon (solid) salts of these acids. Because of their relative abundance, *fluorspar* is used with sulfuric acid to make hydrofluoric, and salt is used to produce hydrochloric acid



At higher temperatures and in the presence of an excess of salt, the second of these reactions goes one step farther



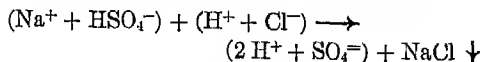
The two acids are gases in their pure states and are, consequently, collected by dissolving them in water. Hydrofluoric acid must be prepared in lead or platinum vessels, which are not readily attacked by the acid,

and the aqueous solution is usually stored in wax containers

The reactions used to produce hydrofluoric and hydrochloric acids are reversible, but under the conditions employed they run to an end in the direction of the hydrogen halide. Equilibrium cannot be attained, because the hydrogen compound of fluorine or chlorine escapes, since the sulfuric acid used is almost free of water, the gases cannot dissolve, and therefore they separate from the other products of the reactions. At the temperature used, sulfuric acid is stable and not volatile. This is the reason for using sulfuric acid instead of nitric acid, for example. If the latter were used in the pure state, its volatility is fairly high even at low temperatures, and it readily decomposes to form gaseous oxides of nitrogen. If it were used, the gaseous hydrogen halide would be impure because of the simultaneous production of other gases, and the reaction would not be as complete.

The reversibility of the reaction of salt and

sulfuric acid can be demonstrated by passing gaseous hydrogen chloride into a saturated solution of sodium hydrogen sulfate (NaHSO_4)



In this reaction the hydrogen chloride does not escape because the water present in the saturated solution of sodium hydrogen sulfate dissolves it. A concentrated solution of hydrogen chloride can, in fact, be used almost as satisfactorily as the gaseous state of the substance. The sodium hydrogen sulfate exists in solution as Na^+ and HSO_4^- or SO_4^{2-} and H^+ ions, the hydrogen chloride forms chloride (Cl^-) and hydrogen ions. Under the conditions specified more sodium and chloride ions are placed in the solution than can be present in a saturated solution of sodium chloride, and hence the excess precipitates as crystals of salt.

41 Commercial Production of Hydrochloric Acid

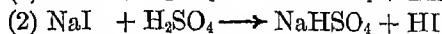
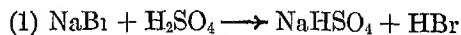
In the oldest, and still widely used, method of producing this acid, an excess of salt is mixed with concentrated sulfuric acid (Figure 174), and the mixture is heated to a moderately high temperature so that sodium sulfate is formed instead of sodium bisulfate. (See the equations in the preceding section.) The sulfuric acid is more fully utilized in

this manner than it would be if the reaction stopped with the formation of sodium sulfate.

Hydrochloric acid is also produced on a commercial scale by the direct combination of hydrogen and chlorine (page 344).

42. Production of Hydrobromic and Hydriodic Acids

We should expect to find that hydrogen bromide and iodide can be prepared in the same manner as hydrogen fluoride and chloride.



When (solid) sodium bromide and sodium iodide are treated with concentrated sulfuric acid, some hydrogen bromide and hydrogen iodide are produced. The products, however, are not pure. In the first reaction (involving the bromide), the gas which is evolved contains considerable quantities of hydrogen bromide, but it also contains free bromine and sulfur dioxide (SO_2). In the second reaction, some hydrogen iodide is present in the gases evolved, but free iodine, sulfur dioxide, and even hydrogen sulfide (H_2S) are also present. The formation of these substances shows that sulfuric acid

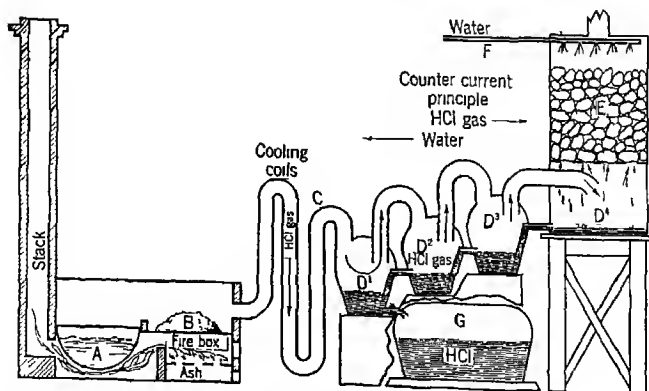


Figure 174. Diagram of a Plant Producing Hydrochloric Acid

A is the retort containing the charge of sulfuric acid and salt, here the salt is converted into sodium acid sulfate. The second reaction is then carried out at B, by heating the mass, which is raked from the retort, directly above the fire box, at B, therefore, sodium acid sulfate is converted into sodium sulfate. The hydrogen chloride is dissolved in the water contained in the jars (D) and in the washing tower (D'). The solution of acid is collected in the receiver G.

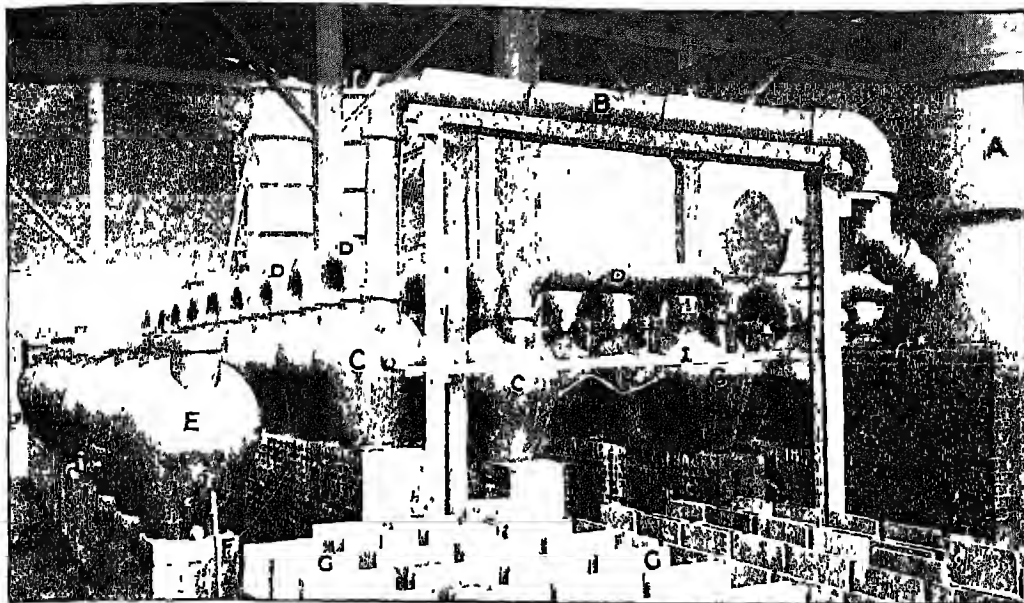
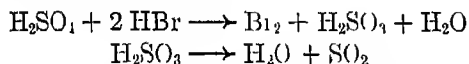


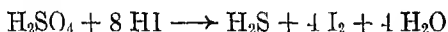
Figure 175. A Hydrochloric Acid Plant

The jars in which the hydrogen chloride is dissolved are called bombannes (C). The gas passes from one bombonne to another through D and finally into the washing tower (A) through B. E and G are storage bombannes and carboys.

oxidizes a portion of the hydrogen bromide and hydrogen iodide:

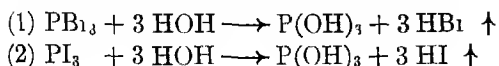


When hydrogen sulfide is formed, the reduction of sulfur is carried still further, since the valence of the element in this compound is -2



Hydrogen bromide and hydrogen iodide are produced commercially by reactions of hydrogen with gaseous bromine and iodine. These reactions are carried out at about 200° with the aid of catalysts, platinum is used in the production of hydrogen bromide and chromic acid in the production of hydrogen iodide.

Pure hydrobromic and hydroiodic acids are usually prepared in the laboratory from phosphorous tri-bromide and phosphorous tri-iodide, respectively. These compounds react with water by double decomposition as follows:



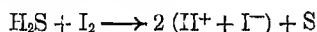
A double decomposition of this type in which water is one of the reacting substances is called *hydrolysis* (page 181). The halides of most of the non-metallic elements, and those of many of the elements usually considered as metals, hydrolyze readily. In general, it is true that the more actively non-metallic the element with which the halogen is combined, the more hydrolyzed is the compound, if it is miscible with water.

In reaction (1), red phosphorus is placed in a limited quantity of water, and bromine is slowly added from a dropping funnel. Bromine reacts readily with phosphorus to form phosphorous tri-bromide, which then reacts with water. The compound P(OH)_3 is phosphorous acid, and its formula is written as H_3PO_3 . The mixture of gases that escapes contains both bromine and hydrogen bromide. The bromine is removed by passing the mixture over phosphorus with which it reacts to form more of the tri-bromide. The hydrobromic acid is then collected by dissolving it in water in which it is very soluble.

In the preparation of hydrogen iodide, iodine and phosphorus are usually allowed to react to form phosphorous tri-iodide by mixing the two

solids and heating them until they melt. Water is then dropped upon the mixture and the reaction takes place as indicated in equation (2). Some iodine escapes with the hydrogen iodide, and this is removed by passing the mixture of gases through a small quantity of water. In most cases the purified hydrogen iodide is collected by dissolving in water, in which it is very soluble.

Hydrogen iodide can be prepared, also, by bubbling hydrogen sulfide through a solution which contains a suspension of iodine or through a solution which is in contact with the solid. The following reaction occurs:



A solution containing 47.5 per cent of hydrogen bromide and boiling constantly at 126° can be prepared by distilling the hydrogen bromide solution resulting from a mixture of *dilute* sulfuric acid and potassium or sodium bromide (saturated). Pure hydrogen bromide is also prepared by the action of bromine upon compounds of carbon and hydrogen. (See similar reactions of chlorine forming hydrogen chloride, page 333.)

43 The Properties of Hydrogen Chloride

Since hydrogen chloride is by far the most widely used and the most important of the hydrogen halides we shall discuss its properties at some length, leaving the three others for briefer discussion in another section (§ 47). Long before the discovery of chlorine, it was known that sulfuric acid reacts upon salt to produce an acid which was called, in the early days of chemistry and by the alchemists, marine or muriatic acid. This name is sometimes still used in referring to the acid as an article of commerce.

The term *hydrogen chloride* now refers to the pure, anhydrous HCl , and the aqueous solution is called hydrochloric acid. As already stated, the modern theory of acids causes us to regard pure hydrogen chloride as an acid, and the distinction between the compound and its solution becomes less important than we once thought. There is considerable difference, however, between dry hydrogen chloride and the solution or

even the moist gas. The two terms, hydrogen chloride and hydrochloric acid, may still be used, therefore, merely for convenience.

Pure hydrogen chloride is colorless and has a very sharp and irritating odor. Under standard conditions a liter weighs 1.6392 g. The molecular weight (36.47) agrees with the formula HCl . It is very stable, as indicated by the small degree of dissociation when it is heated to a high temperature, at 1500°, less than 0.3 per cent is dissociated into hydrogen and chlorine. The gas can be liquefied by decreasing the temperature and increasing the pressure. The liquid is colorless and boils at -85° under one atmosphere of pressure. Its critical temperature is 52° , its freezing point, -111° . The solid is snow-like and crystalline. The anhydrous gas and the liquid are inactive, they do not attack metals at low temperatures, and at high temperatures the dry gas attacks the most active metals only slowly. Neither the liquid nor the anhydrous gas reacts with carbonates or with oxidizing agents as the solution of hydrochloric acid does. The liquid is a non-conductor of the electric current. This is in sharp contrast to the solution, which is an excellent conductor. We may assume, therefore, that pure hydrogen chloride is a covalent compound, and that in solution it reacts with water to form Cl^- and H_3O^+ ions (page 156).

Hydrogen chloride is extremely soluble in water. Its solubility can be demonstrated rather spectacularly as shown in Figure 176. The upper flask is filled with hydrogen chloride. The gas slowly dissolves at first because of the small amount of the water's surface exposed to the gas in the two flasks. As the gas dissolves, the water rises in the tube and finally overflows into the flask containing hydrogen chloride. The gas then dissolves completely and at once, leaving almost a complete vacuum in the upper flask. The pressure of the atmosphere forces the water into this flask. One ml. of water dissolves slightly more than 500 ml. of hy-

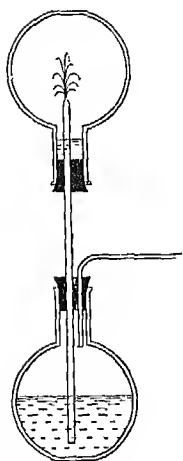


Figure 176. A Method by Which the Solubility of Hydrogen Chloride in Water can be Demonstrated

hydrogen chloride at 0° , and about 455 ml at 15° . The very great solubility of hydrogen chloride in water indicates that a chemical reaction occurs between the solute and solvent (page 156). This is the reaction which produces Cl^- and H_3O^+ ions. A saturated solution at 0° contains slightly more than 39 per cent of HCl . The ordinary "chemically pure" concentrated hydrochloric acid contains about 37 per cent. The constant boiling solution (page 196) contains 20.2 per cent of HCl (760 mm) and boils at 110° , which is the highest boiling point of any aqueous hydrochloric acid solution. The composition varies with the pressure under which the solution boils. This variation indicates that the solution is not a compound.

44 Chemical Properties of Hydrochloric Acid

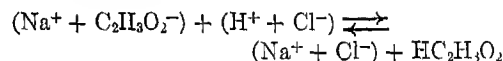
The chemical properties of hydrochloric acid are those of a typical "strong" acid. Like all acids it has a sour taste, turns blue-litmus red and a red (alkaline) solution of phenolphthalein colorless; it is a conductor of the electric current, and it reacts with the oxides and hydroxides of the metals to form salts and water. The properties discussed below are those of many acids and are not specific qualities of hydrochloric acid.

(a) *Action upon Metals* We have referred to the action of certain metals upon hydrochloric

and other acids in discussing the preparation of hydrogen (page 106). All the metals above hydrogen in the electrochemical series act upon hydrochloric acid to liberate hydrogen and form chlorides of the metals. The reaction may be used to produce chlorides such as AlCl_3 , SnCl_2 , and FeCl_2 .

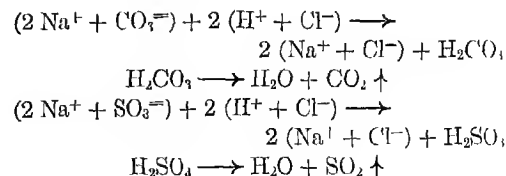
(b) *Action upon Oxides and Hydroxides of the Metals* Acids react with the oxides and hydroxides of the metals to form water and salts. When the acid is hydrochloric, chlorides are formed.

(c) *Action upon Salts* Hydrochloric acid might be expected to react with salts to liberate acids, as sulfuric acid reacts with chlorides to produce hydrochloric acid itself. It does do so, but the reaction is often incomplete because hydrochloric acid itself is volatile and tends to escape from the reacting mixture as a gas. Sulfuric acid, on the other hand, is not volatile at ordinary temperatures, and consequently reacts with salts of volatile acids more completely. When a solution of a salt, such as sodium acetate, is treated with hydrochloric acid, the reaction proceeds to equilibrium.



If solid sodium acetate is treated with concentrated hydrochloric acid, a similar reaction occurs, but the acetic acid which is evolved as a gas, if the mixture is warmed slightly, is impure, being mixed with hydrogen chloride.

Hydrochloric acid does react almost completely, however, with some salts, such as the carbonates and sulfites. The reactions in these cases liberate carbonic and sulfurous acids which are unstable.

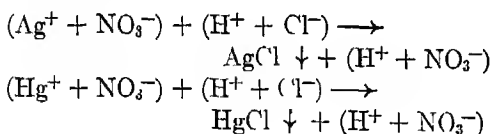


The decomposition of these acids occurs in dilute solutions and at low temperature. Under these conditions there is little loss of hydrogen chloride from the solution by volatilization. Hence the reactions are practically complete in the forward direction.

45. Properties of Hydrochloric Acid Which Are Independent of Its Acid Character

(a) *Action as a Reducing Agent* In discussing the methods of preparing chlorine, the effects of different oxidizing agents upon hydrochloric acid were considered (page 327). Some of the reactions which demonstrate the reducing action of hydrochloric acid are the reactions of manganese dioxide, potassium permanganate, potassium dichromate, and nitric acid

(b) *Action as a Soluble Chloride Test for Chloride Ion* Hydrochloric acid reacts by double decomposition with the soluble salts of certain metals to form the chlorides of the metals. Many of these reactions are far from complete, but silver chloride and mercurous chloride are only slightly soluble and may be easily precipitated by adding hydrochloric acid, or any soluble chloride, to solutions of the nitrates of the two metals. Lead chloride is precipitated in the same manner, but precipitation is never complete owing to the moderately high degree of solubility of lead chloride. All other common chlorides are at least moderately soluble in water



The reaction with silver nitrate is often used as a test for soluble chlorides. The test is regarded as positive when the addition of silver nitrate causes the precipitation of a white, curdy precipitate that turns dark upon exposure to light. Nitric acid may be added to dissolve certain other silver salts which precipitate in a neutral or alkaline solution. This test is not very satisfactory if bromide or iodide ion is present, because silver bromide and silver iodide are also only slightly soluble, even in the presence of nitric acid. These salts are both slightly colored, however, while silver chloride is white.

46. Uses of Hydrochloric Acid

Next to sulfuric acid, hydrochloric is the most widely used acid in industry. It is one of the strongest acids, being considerably stronger than sulfuric. The latter is used more extensively, when a strong or moderately strong acid is desired, because it is cheaper. We should expect hydrochloric acid to cost more than sulfuric, because it is produced by the action of sulfuric acid upon salt. Hydrochloric acid is sometimes less desirable than sulfuric, because it is volatile, and because it acts as a reducing agent. Various concentrations of hydrochloric acid solutions are among the most familiar and most widely used laboratory reagents in analytical chemistry.

Industrially, hydrochloric acid is used in making "pickling" baths for iron that is to be coated with tin or zinc. The acid cleans the surface by removing the coat of oxide. It is also used as a catalyst in the production of syrup from corn starch, it is used in preparing glue from animal tissues such as cartilage, in the manufacture of dyes and drugs, in dissolving the calcium phosphate in bone charcoal, in the manufacture of textiles, and to produce the chlorides of many metals from their oxides, hydroxides, or carbonates.

47. Properties and Uses of the Other Hydrogen Halides

Some of the important properties of hydrobromic, hydriodic, and hydrofluoric acids (and the anhydrous compounds) are given in Table 16. The properties of hydrogen chloride and hydrochloric acid are also tabulated for comparison.

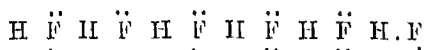
With the exception of hydrogen fluoride, the hydrogen halides have formulas corresponding to HX , as determined by the weight of 22.4 liters of the different gases under standard conditions. The formula of hydrogen fluoride is still somewhat in doubt. When the temperature is around 100° the weight of 22.4 liters (corrected to 0°) of the gas corresponds to the formula HF . At lower temperatures ($30^\circ - 35^\circ$) the correct formula appears to be $(\text{HF})_2$ or H_2F_2 , and at still lower

TABLE 16

Properties of the Hydrogen Halides

Property	HF	HCl	HBr	HI
Solubility in 1 ml. of water at 0°	264 ml (10°)	506 ml.	610 ml	425 ml (10°) fl
Temperature of constant boiling solution (760 mm)	120°	110°	126°	127°
Composition of constant boiling solution	35%	20.2%	47.8%	57%
Boiling point of pure substance	19°	-85°	-67°	-35.5°
Stability — per cent dissociated at 325°	0	1.5×10^{-6}	3.5×10^{-3}	19
Heat of formation (calories) (gas)	38,000	22,030	8,650	-5,926
Strength of the acid	weak	very strong	very strong	very strong

temperatures, $(\text{HIF})_n$. The tendency of simple HF molecules to form molecules such as $(\text{HF})_2$ and $(\text{HF})_n$ may be explained as follows



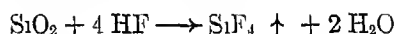
This shows that *hydrogen bonds* (page 183) are responsible for tying together the simple HIF units. At the lower temperatures the more or less complicated molecules are fairly stable, but as the temperature rises and the velocity of the molecules increases, they break up into smaller units.

In dilute solution hydrogen fluoride exists as HF molecules and forms salts such as potassium fluoride, KF , when the acid is neutralized. Acid salts of the type KHIF_2 are also known. At one time, it was thought that the existence of these salts proved that the formula of the acid is H_2F_2 . We are inclined to believe, however, that KHF_2 , and similar acid fluorides, represent the replacement of one hydrogen atom in $\text{H} \ddot{\text{F}} \text{H} \ddot{\text{F}}$ by an atom of potassium or some other metal. This means, of course, that there are some $(\text{HF})_2$ units in a solution of hydrogen fluoride and that these act as a monobasic acid, $\text{H}(\text{HF}_2)$.

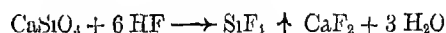
Hydrofluoric acid is a relatively weak acid as compared with the binary acids of the other halogens. Its solution is also a weaker conductor of electricity than the solutions of the other hydro-halogen acids. The weakness of this acid is probably the result of the association of its molecules to form H_2F_2 or H_nF_n , in which hydrogen is more firmly held

and therefore is less available for reactions with bases than it would be in the simple compound HF or as it is in HCl. It is used as a catalyst in the production of high-grade gasoline used as fuel in airplane motors.

Pure hydrogen fluoride and its aqueous solutions react with silica (SiO_2) and silicates, such as calcium silicate (CaSiO_3). The reaction with silica produces silicon fluoride, a gas, and water.



When hydrogen fluoride reacts with metallic silicates, silicon fluoride, water, and fluorides of the metals are produced.



Glass, porcelain, claywares, and similar materials contain silicates. Hydrofluoric acid, therefore, attacks these materials and cannot be stored or allowed to react with other substances in vessels made of them. Its containers are made of lead, platinum, hard rubber, Bakelite, or wax. Beakers in which its solution reacts, and funnels in which it is filtered, must be made of similar materials. Hydrofluoric acid is used to etch glass in making thermometers, graduated cylinders, and burettes. The glass article is coated with paraffin and the portion which is to be etched is exposed by cutting through or scraping away the protecting coat. The article is then exposed to a solution of hydrofluoric acid or gaseous hydrogen fluoride.

Glass is "frosted" by a mixture of hydrofluoric acid and ammonium fluoride. The solution of the acid is used in analytical chemistry to dissolve silicates or materials containing silicates (page 344).

The acid, the pure gas, and all soluble fluorides are very poisonous. Solutions of hydrofluoric acid produce serious burns. Extreme care should be taken not to spill the acid upon the flesh or clothing.

Hydrobromic and hydriodic acids have no extensive uses. They are sometimes used as reducing agents, since they are readily acted upon by many common oxidizing agents. Hydrofluoric acid is not a reducing agent, this is to be expected, since fluorine itself is the most vigorous of all oxidizing agents. Hydrobromic and hydriodic acids, in aqueous solutions, are as "strong" as hydrochloric, but are seldom used as acids because they serve the purpose of an acid no better and are more difficult to prepare than hydrochloric acid.

The iodides and bromides of the metals are soluble with the exceptions of those of silver, mercury (mercurous), and lead. The addition of silver nitrate to a solution of a chloride causes the precipitation of white silver chloride, with a bromide, a light yellowish-tan precipitate of silver bromide is formed; and with an iodide, yellow silver iodide is produced. Silver fluoride is white, and it is much more soluble than the other silver halides. The difference in color of silver chloride, bromide, and iodide may be used in a rough way to determine which of these ions is present in a solution, if only one of them is present. The test is not very definite and for accurate analytical results other methods are used. Each of the halogens, for example, beginning with iodine may be liberated by the proper oxidizing agent (see list, page 362) without affecting those more difficult to oxidize. As iodine and bromine are oxidized they may be extracted by adding several portions of an organic solvent, such as carbon disulfide, in which they are more soluble than in water. The

free halogen may also be expelled by heating or bubbling air through the solution (especially in the case of bromine), until the halogen is completely removed (page 205).

48 Summary Periodic Relations of the Halogens

The structures of the atoms of the four halogens are alike in having seven valence electrons. The negative valence number of each element is consequently 1, and the maximum positive valence number is 7. Fluorine, which has the smallest atomic weight of the family, is the most vigorously reacting non-metal of the entire list of elements. The metallic characteristics increase with increasing atomic weight. This change is indicated by the properties of the elements themselves and those of their hydrogen compounds.

Differences in the chemical behavior of the halogens can be explained by reference to the relative sizes of the atoms of the four elements and the attraction which they have for electrons. The fluorine atom is smallest and attracts electrons most strongly because even the farthest removed electrons of its atoms lie relatively near the nucleus. The iodine atom is the largest, and its valence electrons are farthest removed from the nucleus. Consequently, the iodine atom holds these electrons less firmly and has less attraction for an eighth electron than the atoms of any of the other halogens. It is also easier to separate the electron which the iodine atom acquires, when it becomes an iodide ion, than it is to separate the extra electron from any other halide ion. For this reason hydrogen iodide is a better reducing agent than the other hydro-halogen compounds. Hydrogen fluoride, on the other hand, is not oxidized to free fluorine by any other element, since there is no other element which possesses greater attraction for electrons than fluorine. The attraction of chlorine and bromine atoms for electrons is intermediate between that of fluorine and iodine, the attraction of chlorine being

TABLE 17

Properties of the Halogens

Element	Atomic weight	Melting point	Boiling point	Color and physical state	Boiling point of hydrogen compound	Stability of hydro-acid	Voltage required to ionize atoms (in gaseous state)
Fluorine	19	-223°	-187°	Light yellow gas	19°	stable	16.9
Chlorine	35.46	-102°	-35°	Greenish-yellow gas	-85°	stable	13
Bromine	79.92	-7.3°	59°	Reddish-brown liquid	-67°	unstable	11.6
Iodine	126.92	114°	184°	Purple-black crystalline plates	-35.5	very unstable	8

stronger than that of bromine. The voltage required to ionize the atoms (Table 17) is, in general, a measure of their attraction for electrons.

Review Exercises

1. In what respects is chlorine like oxygen and in what respects do the two elements differ?
2. What volume of chlorine can be produced from 10 liters (standard conditions) of hydrogen chloride by the Deacon process if 75 per cent of the chloride is oxidized?
3. Assuming that there is no loss in the process, what weight of sodium chloride would be required to produce by electrolysis 750,000 tons of chlorine, which is approximately the annual production in this country?
4. What weight of chlorine can be produced by oxidizing HCl (in excess) by one gram-molecular weight each of MnO_2 , KMnO_4 , and $\text{K}_2\text{Cr}_2\text{O}_7$? What weight of chlorine can be prepared by the same reactions using 1000 grams of each of these oxidizing agents?
5. What weight of sodium chloride must be used with an excess of H_2SO_4 and MnO_2 to form one gram-molecular weight of chlorine?
6. What volume of hydrogen chloride (calculated for standard conditions) could be produced from the combination of hydrogen and the chlorine resulting from the electrolysis of 100 grams of sodium chloride? Assume that there are no losses.
7. Describe the variations in the properties of the halogens with increasing atomic weight.
8. Element 85 is a member of the halogen family. What should be its properties? Consider color and physical state, melting and boiling points, vigor of its reaction with hydrogen, oxidizing power, the attraction of its atoms for electrons, its atomic structure, the ease with which the hydrogen compound can be oxidized, and the stability, strength as an acid, boiling point, etc., of the hydrogen compound.
9. Write the equation for the hydrolysis of phosphorus trichloride.
10. What evidence indicates that chlorine is a better oxidizing agent than iodine but a poorer one than fluorine? What evidence indicates that hydrofluoric acid is a weaker acid than hydrochloric?
11. How would you prepare a constant boiling solution of hydrochloric acid? How do we know that this is not a compound of water and HCl ?
12. Compare the properties of pure hydrogen chloride with the properties of its aqueous solution.
13. Suggest a procedure by which the silver iodide used in photography might be prepared.
14. How would you test a solution to determine which acid is present if the solution is known to contain HBr or HI ? How would you prove that the solution contains the acid instead of a salt of the acid?
15. Assuming that Chile saltpeter contains 0.1 per cent of NaIO_3 , what weight of the salt-

peter is required to produce 100 grams of iodine? Assume that there are no losses

- 16 How would you proceed to separate bromine and chlorine from a mixture of the gaseous states of the two substances so that fairly pure samples of each are obtained?
- 17 How is iodine most easily purified?
- 18 What weight of chlorine would be required to liberate all the iodine contained in one liter of a molar solution of sodium iodide if an excess of 10 per cent of chlorine is used? How would you proceed to obtain the released iodine in a fairly pure state?
- 19 For what reason is the production of chlorine by the electrolysis of sodium chloride solutions more satisfactory than the Deacon process?
- 20 Although chlorine reacts with water, it can still be said that chlorine forms a solution in water. Explain how this is possible
- 21 Summarize the chemical behavior of chlorine by writing equations to show how it reacts with metals, phosphorus, sulfur, hydrogen, water, sodium bromide, sodium iodide, hydrogen sulfide, methane, and carbon monoxide
- 22 Under what conditions does the reaction

$$\text{NaCl} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{NaHSO}_4 + \text{HCl}$$
 reach equilibrium? Under what conditions is it most nearly complete toward the right? Toward the left?
- 23 How many liters of normal HCl solution can be prepared from the HCl obtained by treating 100 g of BaCl₂ with concentrated sulfuric acid? Assume that there are no losses
- 24 What volume of chlorine at 22° C and 738 mm will be required to replace completely the bromine in 250 ml of a 0.2 normal solution of sodium bromide?
- 25 What volume of hydrogen bromide (gas) at 0° and 760 mm can be prepared by adding an excess of water to 100 grams of PBr₃?
- 26 Starting with a solution containing sodium iodide and sodium chloride, what oxidizing agent (in the presence of dilute sulfuric acid) could be used to oxidize iodide to free iodine without affecting the chloride? How would

you extract the free iodine from the solution (see page 200)?

- 27 Write equations, using whatever other substances are necessary, to show how you would prepare NaCl from NaBr, Na₂SO₄ from NaHSO₄, HI from H₂S, SiF₄ from SiO₂, HF from CaF₂, HClO from H₂O
- 28 What are the names of the following substances which have been discussed in this chapter? CaOCl₂, HClO, PI₃, S₂Cl₂, SiF₄, CHCl₃, COCl₂, NaHSO₄, CaF₂, Na₃AlF₆, NaIO₃, KMnO₄, K₂C₂O₇, KHF₂, and KI.
- 29 Calculate the volume of molar potassium permanganate solution which would be required to liberate the iodine in one liter of normal hydriodic acid solution
- 30 Complete the following equations and underline all products which would precipitate when aqueous solutions of moderate concentration and containing the reagents indicated are mixed
 - (a) Silver nitrate and potassium iodide
 - (b) Lead nitrate and sodium bromide
 - (c) Barium nitrate and sodium iodide
 - (d) Ferric chloride and mercurous nitrate
- 31 Describe the changes which would occur in the composition of the solution in the flask and in the distillate during the distillation of a solution containing 30 per cent of hydrogen chloride
- 32 One ml of liquid bromine weighs 3.18 times as much as 1 ml of water. What volume of liquid bromine would be required, if it were completely converted into HBr, to produce one liter of a solution of the same concentration as could be produced by dissolving 44.8 liters (standard) of hydrogen chloride in a liter of water?
- 33 What is the weight of one liter of hydrogen iodide (gas) calculated for 0° and 760 mm?
- 34 Using the electronic theory of atomic structure, explain why (1) fluorine is a better oxidizing agent than chlorine, and (2) iodide ion is easily oxidized to free iodine.

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OXIDATION AND REDUCTION; BALANCING EQUATIONS

1 Introduction

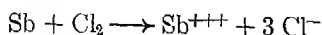
Oxidation and reduction have been explained in Chapter 6. In this chapter we are to study the methods used to balance equations representing chemical changes of this kind and the relative activities or powers of different oxidizing and reducing agents.

EQUATIONS FOR OXIDATION-REDUCTION REACTIONS

2. The Reaction of Antimony and Chlorine

Balancing an equation for the reaction that occurs between an oxidizing and a reducing agent calls essentially for a balance of the loss in valence number of one element against the increase in the valence number of the other. The valence number of one is reduced as much as that of the other is increased. The problem of balancing the equation, therefore, is really one of determining the numbers of atoms of each element that must be shown in the equation in order that the total change in the valence number for one will be equal to the total change for the other element.

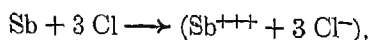
Let us consider a simple example of oxidation and reduction. Antimony, Sb, reacts with chlorine, Cl_2 , to form antimony trichloride, SbCl_3 .



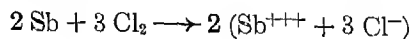
Element oxidized, Sb Change in valence number from 0 to +3, a gain of 3	Element reduced, Cl Change in valence number from 0 to -1, a loss of 1 per atom
--	--

How many atoms of antimony and mole-

cules of chlorine must be shown in the equation? The correct numbers will be those that will make the total gain in the valence number of antimony equal to the decrease in the valence number of chlorine. Since each atom of antimony undergoes a change of +3 in valence number, and each atom of chlorine a change of -1, it is evident that three atoms of chlorine must be used in order that chlorine will show as much decrease as one atom of antimony increases or, in other words, three atoms of chlorine must be used to remove three electrons from one atom of antimony. Hence, we could write our equation as



but for the fact that chlorine exists as molecules of Cl_2 and not as single atoms. Therefore, in order that the equation will show this fact, we must double the quantity of each substance



3. What Substances are Produced?

We cannot write any equation unless we know the substances produced, and if more than one valence, or oxidation, state of any of the elements involved are possible, we must also know which of these are represented in the original substances and in the products. It is not enough to know that iron is oxidized by chlorine. Before we can write the equation, we must know whether the iron produced is Fe^{++} or Fe^{+++} .

Sometimes, the products of a reaction can

be predicted almost, if not completely, with certainty from a knowledge of the chemical properties of the substances involved. For example, several metals have but one valence number — besides 0, of course — and, therefore, there can be no uncertainty as to the changes that involve their oxidation or reduction. Calcium in its compounds always has a valence number of +2, and hence, when metallic calcium is oxidized it can form only Ca^{++} ion, and when this ion is reduced, it can form only metallic calcium. It is also helpful to remember that hydrogen always has a valence number of +1, except in a few hydrides of metals, such as LiH , in which its valence number is -1, that oxygen's valence number is -2, and that chlorine in compounds with the metals or hydrogen always has a valence number of -1.

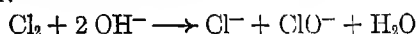
For elements like iron that have two or more valence-states the chemist must sometimes rely upon laboratory tests to determine what substance is produced in a reaction. If iron oxidizes iron by means of chlorine, bromine, iodine, or some other oxidizing agent, either Fe^{II} or Fe^{III} is produced, and it is not always the same ion. The chemist can easily decide which ion is produced by a simple test that gives one result if the ion is Fe^{II} and another if it is Fe^{III} . Upon adding potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, to a solution containing iron ions and hydrochloric acid, a dark blue precipitate of $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ is formed if Fe^{++} is present, a white precipitate of $\text{Fe}_2\text{Fe}(\text{CN})_6$ forms if Fe^{++} , but no Fe^{+++} , is present. A similar dark blue precipitate of $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ is produced by adding potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, if Fe^{++} instead of Fe^{+++} has been formed.

When sulfur in H_2S (valence number of sulfur, -2) is oxidized, (a) free sulfur (valence number, 0), (b) sulfite ion, SO_3^{--} , or sulfur dioxide, SO_2 (valence number, +4), or (c) sulfate ion SO_4^{--} or sulfur trioxide, SO_3 (valence number, +6) may be formed. If free sulfur is formed, it will appear as a solid insoluble in water. To distinguish between SO_3^{--} and SO_4^{--} , barium chloride may be added to form a precipitate of BaSO_3 or BaSO_4 . If it is the former, the precipitate will dissolve when hydrochloric acid is added, if the latter, the precipitate will not dissolve in the acid.

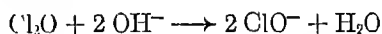
We may mention other simple facts that may well be kept in mind in writing equations for reactions in which changes in valence states occur.

(1) We should not expect an active metal to be produced by the reduction of its ions in the presence of water. Sodium, for example, reacts with water to form sodium hydroxide and cannot, therefore, be reduced from Na^+ to Na in an aqueous solution.

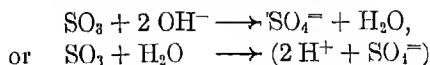
(2) We should not expect the oxide of a metal to be produced in a reaction if an acid is present. Thus, the oxidation of copper by sulfuric acid does not produce cupric oxide, CuO , because this oxide will react with the acid to produce cupric sulfate, $\text{Cu}^{++}\text{SO}_4^{--}$, and water. Similarly, the oxide of a non-metal will not be produced in the presence of a hydroxide-base, such as NaOH . If chloride ion, Cl^- , for example, is oxidized in the presence of OH^- ion, it should not be expected to form free chlorine or an oxide of chlorine. Free chlorine will not be formed, because it reacts (page 335) with hydroxyl ion.



The oxide should not be expected, for, since it is the anhydride of an acid, it will react with hydroxyl ion to form a salt, or the ions of a salt.



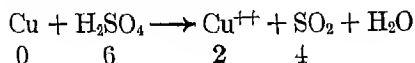
Likewise, sulfur when oxidized in the presence of OH^- , or even in water, to a valence number of +6, forms not the oxide, SO_3 , but the sulfate, SO_4^{--} ion, because SO_3 is the anhydride of sulfuric acid.



In the equations that we shall consider in this chapter, information concerning the products of the reaction will be given. Later, when the student has had more experience with the chemical properties of the substances involved, he may, for many reactions, be able to determine the products of the reaction for himself.

4. The Oxidation of Copper by Sulfuric Acid

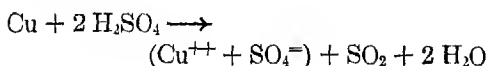
The products of this reaction are Cu^{++} , sulfur dioxide, SO_2 , and water. Let us first write a tentative equation, and under the elements that are oxidized and reduced let us write their valence numbers before and after the change occurs



Oxygen and hydrogen do not undergo any change involving their valence numbers. The changes for copper and sulfur are

	Copper	Sulfur
Change in valence	0 to +2,	+6 to +4,
number per atom	gain of 2	loss of 2

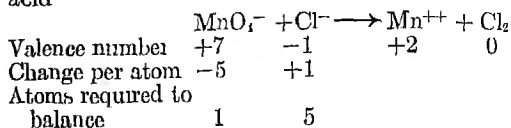
Since each sulfur atom loses as much in valence number as each copper atom gains, the equation is balanced by using one atom of each, and since there is one atom of sulfur in a molecule of sulfuric acid, only one molecule of that substance is required. The equation, therefore, may be allowed to remain in the tentative form that we first wrote. But if we wish to indicate a sulfate ion, SO_4^{--} , which will go along in the solution with the Cu^{++} ion to make a complete set of the ions of cupric sulfate, one more molecule of sulfuric acid must be added on the left to supply this ion. If we do this, the equation becomes



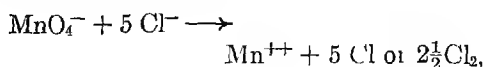
5. Oxidation of Hydrochloric Acid by Potassium Permanganate

Let us next turn to a reaction that has been used (page 328) to produce chlorine, namely the oxidation of hydrochloric acid by potassium permanganate. To balance this equation we must know that manganese is reduced to Mn^{++} and that chlorine is oxidized to Cl_2 . With this information before us we should be able to balance the equation. Any permanganate will act in the same manner. It is actually only the

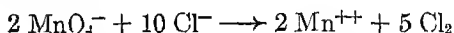
permanganate, MnO_4^- , ion that is involved, and we may, for the time being at least, omit the potassium ion and, for the same reason, the hydrogen ion of the hydrochloric acid



Therefore, we may write the equation as

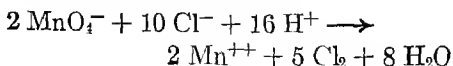


or, to show a whole number of *molecules* of chlorine, as



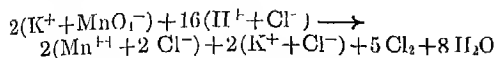
The equation is not yet complete, however, because we have not shown what becomes of the oxygen in the two MnO_4^- ions. Manganese, after the reaction, cannot appear as the oxide, MnO , because this is a basic oxide, and the solution contains an acid, HCl . The hydrogen ions of this acid are the only substances in the entire mixture that can react with the oxygen of MnO_4^- , therefore, we must add on the left a sufficient number of H^+ ions to react with all the oxygen in two MnO_4^- ions. To determine the number of H^+ ions that must be added, there are two possible procedures. First, consider the difference in the charges on the left and on the right. On the right the total charge is $2 \times (+2)$ or $+4$, and on the left it is $(-2) + (-10)$ or -12 . To equalize these we must add 16 $+$ charges on the left, and since each hydrogen ion has a charge of $+1$, 16 H^+ ions are required. We can arrive at the same conclusion by noting that the 8 atoms of oxygen in the two MnO_4^- ions require 16 atoms of hydrogen and will form 8 molecules of water.

Our equation now becomes



If we wish to fill in the equation with missing ions to make complete sets with

Mn^{++} , MnO_4^- , Cl^- , and H^+ ions we may write



All that has been done in this final step is to add 6 Cl^- ions (2 for the potassium, K^+ , ions and 2 each for the two Mn^{++} ions) on the right-hand side of the equation and the same number of Cl^- ions on the left.

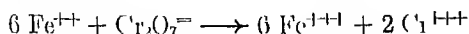
6 Oxidation of Ferrous Sulfate by Sodium Dichromate

Let us next consider the oxidation of ferrous ion, Fe^{++} , to ferric ion, Fe^{+++} , by the dichromate ion, $\text{Cr}_2\text{O}_7^{--}$. As reagents we may use FeSO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7$. The dichromate ion is converted by this reaction into chromic ion, Cr^{+++} , which is about the only change that can occur for chromium, which has only two important valence numbers, +3 and +6, in a few rare compounds it has a valence number of +2.

Using the same procedure to balance the equation as in the preceding examples, we write first

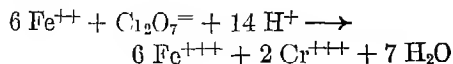
	$\text{Fe}^{++} + \text{Cr}_2\text{O}_7^{--} \longrightarrow \text{Fe}^{+++} + \text{Cr}^{+++}$			
Valence number per atom	+2	+6	+3	+3
Change in valence number per atom	+1	-3		
Atoms required to balance	3	1		

Since there are two atoms of chromium in each $\text{Cr}_2\text{O}_7^{--}$ ion, it is obvious that 6 atoms of iron, or 6 Fe^{++} , must be indicated on the left and 2 Cr^{+++} ions on the right. Hence,

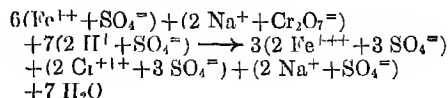


Electrical charges	$(6 \times 2) + (-2) = +10$	$(6 \times 3) + (2 \times 3) = +24$
Number of H^+ to be added	14	

Therefore,



If we now add to the equation the 2 Na^+ ions for $\text{Cr}_2\text{O}_7^{--}$, 6 SO_4^{--} ions for 6 Fe^{++} , and 7 SO_4^{--} ions for 14 H^+ on the left, and 9 SO_4^{--} ions for 6 Fe^{+++} , 3 SO_4^{--} ions for 2 Cr^{+++} , and (2 $\text{Na}^+ + \text{SO}_4^{--}$) on the right we show all the ions as complete sets.



The requirement of 14 H^+ ions on the left-hand side of this equation explains why the reaction must be carried out in an acid solution. As a matter of fact, $\text{Cr}_2\text{O}_7^{--}$ ion exists only in acid solution.

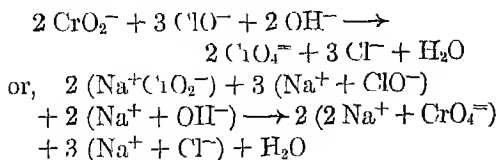
7. Oxidation in an Alkaline Solution

The hydroxide of chromium, when the valence number of chromium is +3, is $\text{Cr}(\text{OH})_3$. This hydroxide reacts as an acid ($\text{H}_2\text{CrO}_3 - \text{H}_2\text{O} = \text{HCrO}_2$) with sodium hydroxide and forms sodium chromite, NaCrO_2 . This substance is oxidized by sodium hypochlorite, NaClO , to sodium chromate, Na_2CrO_4 , but only in an alkaline solution. The hypochlorite ion, ClO^- , is reduced at the same time to Cl^- ion. Free chlorine should not be expected as the product of the reaction (page 357), because chlorine reacts with hydroxyl ion to form Cl^- and ClO^- ions.

	$\text{CrO}_2^- + \text{ClO}^- \longrightarrow \text{CrO}_4^{--} + \text{Cl}^-$			
Valence number per atom	+3	+1	+6	-1
Change in valence number per atom	+3	-2		
Atoms required to balance	2	3		

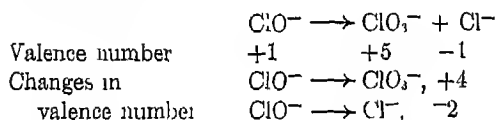
	$2\text{CrO}_2^- + 3\text{ClO}^- \longrightarrow 2\text{CrO}_4^{--} + 3\text{Cl}^-$			
Electrical charges	$(2 \times -1) + (3 \times -1) = -5$	$(2 \times -2) + (3 \times -1) = -7$		
Negative charges to be added	2			

The negative charges required on the left are supplied by adding 2 OH⁻ ions

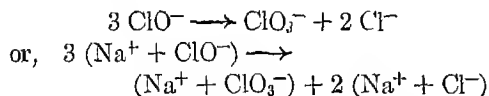


8 A Reaction in which the Same Element is both Oxidized and Reduced

When it reacts with hydroxyl ion, chlorine is reduced to chloride ion, Cl⁻, and it is also oxidized to hypochlorite ion, ClO⁻, in which its valence number is +1. However, we shall consider a somewhat more complicated example of a similar change, namely the conversion of sodium hypochlorite, when it is heated, into sodium chloride and sodium chlorate. Let us consider only the ions containing chlorine

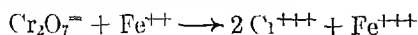


The loss and the gain in valence number are equalized only when 2 ClO⁻ ions are reduced to Cl⁻, and hence it is evident that for each ClO⁻ ion converted into ClO₃⁻ two ClO⁻ ions must be converted into Cl⁻ ions. Hence,

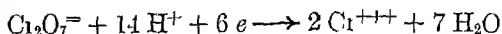


9 The Ion-Electron Method of Balancing Equations for Oxidation-Reduction Reactions

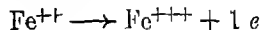
This method of balancing equations gives the same results as the method already described and is preferred by some. It depends essentially upon the determination of the number of *electrons transferred* from the reducing agent to the oxidizing agent in the reaction. To illustrate this method let us consider the reaction (page 359) of dichromate ion with ferrous ion



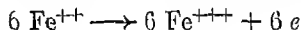
Let us look separately at the oxidation and reduction. The reduction is shown by $\text{Cr}_2\text{O}_7^{2-} \longrightarrow 2 \text{Cr}^{+++}$, and the oxidation by $\text{Fe}^{++} \longrightarrow \text{Fe}^{+++}$. Now when $\text{Cr}_2\text{O}_7^{2-}$ is reduced, 14 H⁺ must be added to react with the 7 atoms of oxygen to form water: $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \longrightarrow 2 \text{Cr}^{+++} + 7 \text{H}_2\text{O}$. The net charges are +12 on the left and +6 on the right. To balance these we must add 6 electrons, indicated by 6 e⁻, on the left. Hence, for this portion of the equation we have



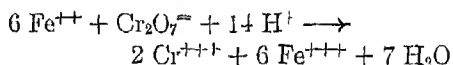
Now for the other part of the equation one electron must be added on the right to balance the charges



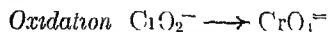
The two portions of the equation now show that the first half must obtain 6 electrons from the second half, which as written gives up only one. Therefore, the quantities in the second half must be multiplied by 6.



If we now add the two halves of the equation and cancel out 6 e⁻, which occur on both sides, we obtain

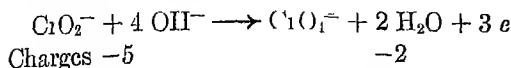


Let us balance by the same method the equation (page 359) for the oxidation of ClO_2^- to CrO_4^{2-} by ClO^- in the presence of OH⁻

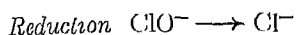


Two oxygen atoms are required to form CrO_4^{2-} , since ClO_2^- contains but two, and 2 OH⁻ will be required to provide them. However, we need some oxygen left over to form water with the hydrogen of the OH⁻ ions, hence we must use more than 2 OH⁻. Three OH⁻ ions will not do, because this would give three atoms of hydrogen and only one of oxygen. Four OH⁻ ions must be used, because they will provide oxygen

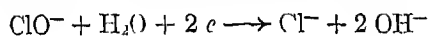
atoms to change CrO_2^- to CrO_4^{2-} and also two to form water with the four atoms of hydrogen. Hence,



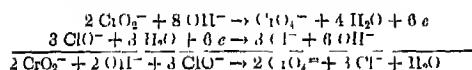
Three electrons must be added on the right to balance the charges.



The oxygen atom of the ClO^- ion must be taken care of in some way, and the only way in which this can be done in an alkaline solution is by means of a molecule of water with which it will form 2OH^- ions. For this half of the equation we may write



Two electrons are required to balance the charges. This half of the equation requires two electrons and the first half provides three. Hence, to balance one half against the other, we multiply the second half by three and the other half by 2, add, and cancel out the electrons.

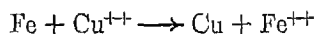


OXIDIZING AND REDUCING AGENTS

10 The Relative Oxidizing and Reducing Powers of Different Substances

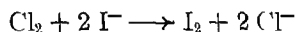
On several occasions in early chapters we have referred to the different degrees of attraction that atoms of different elements have for electrons. The large atoms of the alkali metals—large as compared to atoms of other elements in the same periods as themselves—possess relatively weak attraction for their valence electron and, therefore, they are readily converted into positive ions, i.e., they are very active reducing agents. Atoms of the halogens, on the other hand, have strong attraction for electrons, and therefore, acting as oxidizing agents, they remove electrons from other atoms and become negative ions. Since

oxidation and reduction involve losses of electrons by some atoms and acquisitions by others, it should be possible to arrange the elements in a table according to their relative attraction for electrons and, therefore, according to their oxidizing and reducing powers. Such a table can be determined by more accurate methods, but at least a satisfactory comparison can be made by determining other elements that each element will replace from their compounds. For example, iron will replace copper from a solution containing Cu^{++} ions, hence copper must have more attraction for electrons than iron, because an atom of copper removes two electrons in this reaction from each atom of iron.



Therefore, when copper and iron are listed in the order of their powers or strengths as reducing agents, iron should be placed above copper, and when listed as oxidizing agents cupric ion comes before ferrous ion.

Chlorine replaces iodine from solutions containing I^- ions, hence chlorine atoms must possess stronger attraction for electrons than iodine.



Therefore, in a list of oxidizing agents chlorine is placed above iodine. Of the two ions Cl^- and I^- , the latter is more easily oxidized to the free element and therefore is the stronger reducing agent. Sulfuric acid will oxidize I^- to I_2 , for example, but it does not oxidize Cl^- .

By similar comparisons, and by studying the effects of different oxidizing agents upon the same reducing agents, we can compile a list in which many substances, in addition to the metals, the non-metals, and their ions, are arranged in the order of their oxidizing and reducing powers. Table 18 includes many of the common oxidizing and reducing agents arranged in this manner. For the elements we can predict the order on the basis of the atomic radii of their atoms, then

ionization potentials, and the number of electrons in the outermost shells of the ions (page 54, see also page 269)

TABLE 18

Some of the Common Oxidizing Agents Arranged in the Order of Their Strengths¹

Fluorine
Ozone
Cobaltic chloride, CoCl_3
Hypochlorous acid, HClO
Potassium chlorate, KClO_3
Lead dioxide, PbO_2
Potassium permanganate, KMnO_4
Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$
Nitric acid, concentrated
Chlorine
Sulfuric acid, concentrated and hot
Oxygen
Sodium iodate, NaIO_3
Bromine
Silver ion, Ag^+
Ferric chloride, FeCl_3 , and other ferric salts
Iodine
Sulfur
Stannic chloride, SnCl_4

¹ This list is not complete, nor are the positions of the different substances very definite. Changes in concentration, temperature, and other conditions sometimes cause changes in the relative oxidizing actions of different substances and, therefore, changes in the order of the positions in this list. The concentration of acid that is present in a mixture in which the oxidizing agent reacts is very often an important factor in determining the oxidizing strength of a substance and, also, in determining the extent to which the same substance is reduced. The effect of the acid is particularly noticeable in the action of lead dioxide, nitric acid, potassium permanganate, and potassium dichromate.

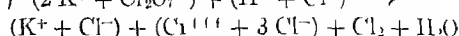
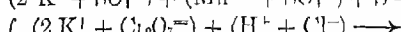
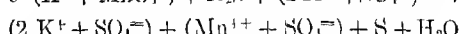
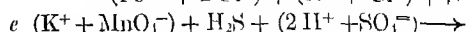
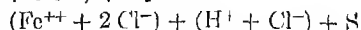
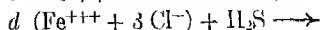
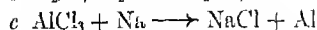
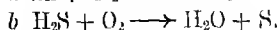
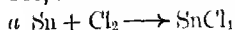
11 Speed of Oxidation

The speed with which one substance oxidizes another is no true measure of the oxidizing power of that substance. Speed depends upon many factors (page 80) that do not enter into the determination of oxidizing power. Chlorine, for example, has greater oxidizing power than iodine (page 341), because iodine oxidizes iron only to Fe^{++} ion, whereas chlorine oxidizes it to Fe^{+++} . The speed with which iron is oxidized by iodine, however, may be greater than that of the action of chlorine upon iron,

i.e., more iron may be oxidized in the same time by iodine, but it is not oxidized as far

Review Exercises

1 Using the method illustrated on pages 358-360, balance the following equations

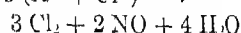
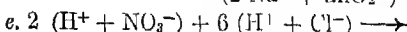
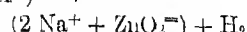
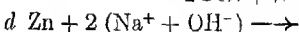
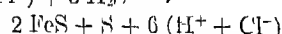
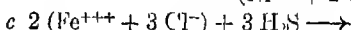
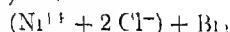
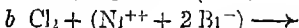
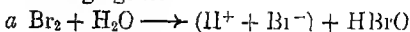


2 In each of the reactions of (1) name the oxidizing agent and the reducing agent

3 What weight of chlorine is required to liberate 10 g. of iodine from sodium iodide?

4 Chlorine can be produced by the action of hydrogen chloride upon potassium permanganate. What is the maximum quantity of chlorine that can be produced from 13 g. of potassium permanganate by this reaction?

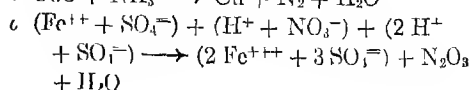
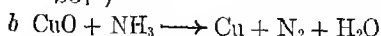
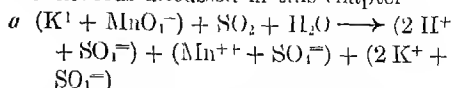
5 In the following reactions what elements are oxidized and what substances act as the oxidizing agents?

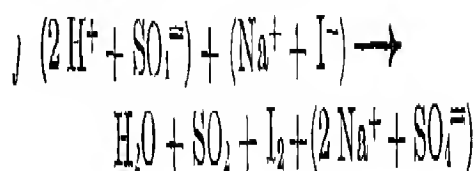
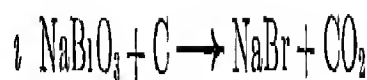
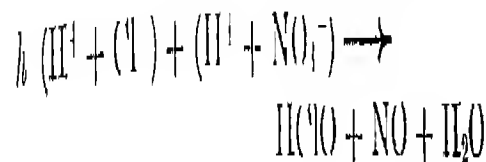
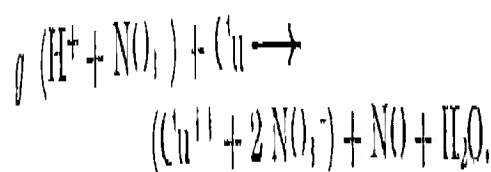
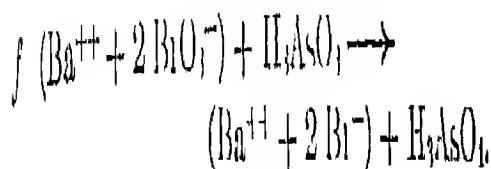
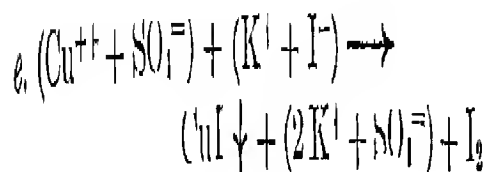
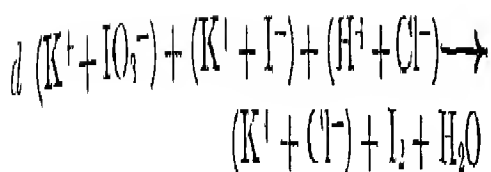


6 What changes in valence numbers occur in each of the equations of (5)?

7 What are the valence numbers of the underlined elements in $\underline{\text{C}}(\text{O})_2$, $\underline{\text{P}}(\text{O})_3$, $\underline{\text{S}}(\text{O})_2$, $\underline{\text{Cr}}(\text{O})_2$, $\underline{\text{N}}\text{O}_3^-$, $\underline{\text{B}}\text{O}_3$, $\underline{\text{As}}\text{O}_4^{--}$, and $\underline{\text{Mn}}\text{O}_4^{--}$?

8 Balance the following equations by any of the methods discussed in this chapter





References for Further Reading

Balancing Oxidation-Reduction Equations

J Chem Ed 3, 1305 (1926), 4, 1021, 1159 (1927), 6, 1136 (1929), 12, 189 (1935), *Sch Ser and Math*, 41, 419 (1941)

THE OXYGEN COMPOUNDS OF THE HALOGENS

Chlorine, though formerly called an acid, possesses no acid properties. Its strong affinity for the metals is sufficient proof that it is not an acid, for chemists are not acquainted with any instance of direct combination between an acid and a metal.

TURNER, "THE NATURE OF CHLORINE," 1828

1. Introduction

Oxygen compounds of all four halogens are known. In addition to their oxides chlorine, bromine, iodine, and possibly fluorine form oxygen acids, such as HClO_3 , at least in aqueous solution, and salts of these acids, e.g., KClO_3 . Some of the salts are important substances, but the oxides are of little importance.

The oxides of chlorine are Cl_2O , Cl_2O_6 , ClO_2 , and Cl_2O_7 , of bromine, Br_2O , Br_2O_3 , and Br_2O_5 , of iodine, I_2O_4 , I_2O_5 , and I_2O_7 , and for fluorine, two oxygen compounds

have been prepared, F_2O and F_2O_2 . The oxygen acids of the halogens and their anhydrides, some of which are only hypothetical substances, are listed in Table 19.

PREPARATION AND PROPERTIES OF THE OXIDES OF CHLORINE

2. Chlorine Monoxide (Cl_2O)

Chlorine monoxide is a yellow gas, which explodes violently, condenses to a liquid at about 4° , and reacts with water to form hypochlorous acid. It can be prepared by distilling a solution

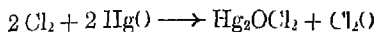
TABLE 19

The Oxygen Acids of the Halogens *

Anhydride	Name	Formula	Name
Cl_2O	Chlorine monoxide	HClO	Hypochlorous acid
(Cl_2O_3)	Chlorine trioxide	HClO_2	Chlorous acid
(Cl_2O_5)	Chlorine pentoxide	HClO_3	Chloric acid
Cl_2O_7	Chlorine heptoxide	HClO_4	Perchloric acid
Br_2O	Bromine monoxide	HBrO	Hypobromous acid
(Br_2O_3)	Bromine pentoxide	HBrO_3	Bromic acid
(I_2O)	Iodine monoxide	HIO	Hypoiodous acid
I_2O_5	Iodine pentoxide	HIO_3	Iodic acid
(I_2O_7)	Iodine heptoxide	HIO_4	Periodic acid
		(H_5IO_6)	Periodic acid
F_2O	Fluorine monoxide or Oxygen fluoride	$(\text{HFO}?)$	Hypofluorous acid

* The compounds enclosed in parentheses are hypothetical only, or they are so unstable that they exist only momentarily as intermediate steps in the formation or decomposition of other compounds.

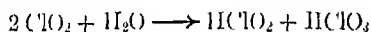
of hypochlorous acid (HClO) under reduced pressure, or by passing chlorine over mercuric oxide



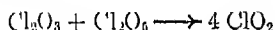
A portion of the chlorine is oxidized in this reaction to a positive valence of 1 in Cl_2O , and a portion is reduced to a negative valence of 1 in Hg_2OCl_2

3. Chlorine Dioxide (ClO_2)

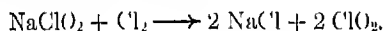
Chlorine dioxide is a yellow gas, which decomposes explosively into chlorine and oxygen, condenses to a liquid at about 10° , and reacts with water to give both chlorous and chloric acids



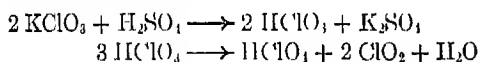
This behavior indicates that chlorine dioxide is a mixed anhydride, it acts as if it consists of both Cl_2O_3 and Cl_2O



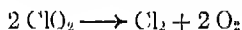
It is produced by the action of chlorine upon dry sodium chlorite, NaClO_2



Whenever a chlorate is treated with a strong acid, such as sulfuric, chloric acid is liberated and then quickly decomposes



The chlorine dioxide then decomposes, explosively if the mixture is slightly warmed

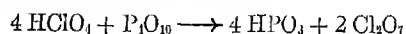


Because of the violence attending this reaction, it is very dangerous to add sulfuric acid, or any other strong acid, to a solid chlorate or any material likely to contain a chlorate. Chlorine dioxide, greatly diluted with air, is now used as a bleaching agent for flour and certain fabrics

4. Chlorine Heptoxide (Cl_2O_7)

Chlorine heptoxide is a colorless, oily liquid which explodes violently when heated or when jared roughly. It is more stable than the other oxides of chlorine and at low temperatures can be brought into contact with easily oxidizable materials, such as phosphorus, without immediate reactions occurring. It is the anhydride of per-

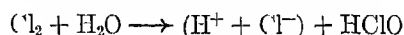
chloric acid (HClO_4) and can be prepared by removing the water from this acid by means of phosphorus pentoxide (P_2O_5)



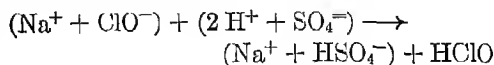
THE OXYGEN ACIDS OF CHLORINE AND THEIR SALTS

5 Hypochlorous Acids and the Hypochlorites

In discussing the properties of chlorine (page 334) we have already learned that the element reacts with water to form both hydrochloric and hypochlorous acids



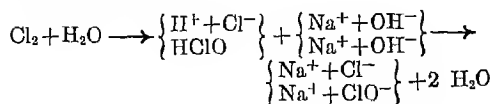
This reaction is reversible, hence, the hydrochloric acid must be removed without affecting the hypochlorous acid if the latter is to be produced in any considerable quantity. This may be done by adding powdered limestone, or calcium carbonate, with which the hydrogen chloride reacts readily, to the water into which the chlorine is passed. Hydrochloric acid reacts with calcium carbonate (page 301), but hypochlorous acid, which is very weak, does not. If the solution resulting from this treatment is distilled, a dilute solution of hypochlorous acid is obtained as the distillate. It may also be prepared, in a similar state, by distilling a mixture containing dilute sulfuric acid, sodium chloride, and sodium hypochlorite. In the dilute acid solution, sodium hypochlorite is converted into the weak acid, HClO , and NaHSO_4 .



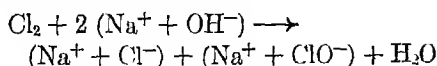
while the sodium chloride is not affected. Pure, dry hypochlorous acid has not been prepared, owing to its extremely unstable nature. The acid is known only in solution.

The mixture of sodium chloride and sodium hypochlorite which is mentioned in the paragraph above can be prepared by passing chlorine into a cold solution of sodium hydroxide. We may think of the reaction as proceeding, first, as indicated

above for chlorine and water, and secondly, as a reaction in which the base neutralizes the two acids

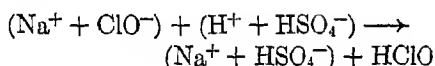


These equations may be combined as follows



The neutralization of the acids causes the reaction between chlorine and water to run almost completely to the right, and all of the chlorine may be consumed if sufficient sodium hydroxide is added

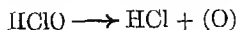
The solution that contains sodium chloride and sodium hypochlorite is called *Javelle water*. When a solution containing a small concentration of hydrogen ion — a dilute solution of a strong acid or a more concentrated solution of a weak acid — is added to this solution, hypochlorous acid is liberated again



Since hydrochloric acid exists in solution almost entirely as ions, the hydrogen ions that are added do not combine with chloride ions to form molecules of HCl . On the other hand, hypochlorous acid — a weak acid — exists largely as molecules of HClO ; it does not form many ions. Hence, when hydrogen and hypochlorite ions, ClO^- , are brought together in the same solution, they combine to form molecules of the acid. If a more concentrated solution of a strong acid is added — supplying a large number of hydrogen ions — the ions of hydrochloric acid and molecules of hypochlorous acid react to form chlorine and water. This reaction is the reverse of the one between chlorine and water. To show that the reaction is reversible, we can write it, using two arrows, as follows.

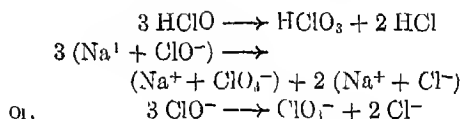


In the presence of substances which are readily oxidized, hypochlorous acid reacts as follows



The oxygen is liberated in the atomic form, which is sometimes called the *nascent* state — the state of “being born.” Thus oxygen is a much more vigorous oxidizing agent than ordinary gaseous oxygen for two reasons: (1) The dissociation of the oxygen molecule (O_2) is an endothermic reaction requiring energy to bring it about, whereas nascent oxygen is already in the dissociated state, (2) the decomposition of hypochlorous acid, which produces nascent oxygen, is exothermic and hence, instead of requiring energy, actually liberates energy which may be instrumental in promoting the oxidizing action of the oxygen which is liberated. The bleaching action of chlorine and the fact that water is required for this bleaching action are explained by this reaction. When hypochlorous acid decomposes in the sunlight and in the absence of oxidizable materials, ordinary gaseous oxygen (O_2) is produced, or the acid may decompose to some extent to form chlorine monoxide.

When solutions containing hypochlorous acid or a hypochlorite, such as NaClO , are heated, chloric acid or a chlorate is produced



A portion of the chlorine is reduced to a negative valence number of 1, Cl^- , and a portion is oxidized to a positive valence number of 5, ClO_3^- . Potassium chlorate can be produced in the same manner as sodium chlorate if potassium hydroxide is substituted for sodium hydroxide in neutralizing the acids formed when chlorine and water react.

A solution containing sodium chloride and sodium hypochlorite may be prepared, also, by electrolyzing a solution of sodium chloride under conditions which allow the chlorine that is liberated at the anode to react with the sodium hydroxide that collects around the cathode. This is the opposite of the condition which we strive to obtain when we wish to prepare chlorine and pure sodium hydroxide by the same process.

When the chlorine is allowed to react with sodium hydroxide, the reactions are the same as when chlorine is bubbled through a solution of sodium hydroxide. Mixing is secured by using a stirrer in the solution during electrolysis. Low temperatures are used to prevent the formation of chlorates.

6. Uses of Sodium Hypochlorite

Sodium hypochlorite, usually as a solution containing sodium chloride, has several uses. It is employed extensively to remove (by oxidation) the ill-smelling compounds of sulfur which are often found in gasoline and kerosene. It is used still more extensively in the bleaching of certain kinds of cloth. The bleaching process is shown in Figure 177. The cloth which is to be bleached is first passed over rollers and through a solution of sodium hydroxide or lime water (calcium hydroxide). The cloth then passes continuously into a tank containing a dilute solution of an acid, which neutralizes the excess of the base, and next into a solution of sodium hypochlorite or a suspension of "bleaching powder" which is, in part (page 368), calcium hypochlorite. The cloth is next treated with an acid again, this time to react with the hypochlorite and to liberate hypochlorous acid, which is the substance responsible for the bleaching action. The excess of chlorine and hypochlorous acid must be removed to prevent them from weakening the cloth, which, therefore, is passed through a tank containing an "antichlor." A solution of sodium thiosulfate is

often used for this purpose. This step converts the chlorine into sodium chloride. The cloth is then washed in water and passed through a drying chamber in which heated air is circulated. Javelle water is used in some laundries to bleach discolorations that are not removed by the usual procedure. Certain kinds of cloth, such as cotton, are not much affected by the hypochlorite and may be washed in a solution containing a moderate amount of this substance without any appreciable injury to the fabric. Wool and silk are rapidly weakened and soon destroyed by the same solution. Small containers of a solution of sodium hypochlorite and sodium chloride are sold under trade names for use in laundry work in the home. The Javelle water which they contain is usually prepared by the electrolysis of a sodium chloride solution. It should not be used in laundering wool and silk fabrics.

Solutions of hypochlorites, usually a solution of sodium chloride and sodium hypochlorite, are sold under various names as antiseptics. If freshly prepared, or if the hypochlorite is stabilized in some manner, they are among the best of the substances used for this purpose. Because it is important that they contain no injurious ingredients, such as sodium hydroxide, they must be carefully prepared. The well-known Carrel-Dakin solution, an antiseptic of this kind, was introduced and widely adopted during the first World War in treating wounds. It proved decidedly more effective than former

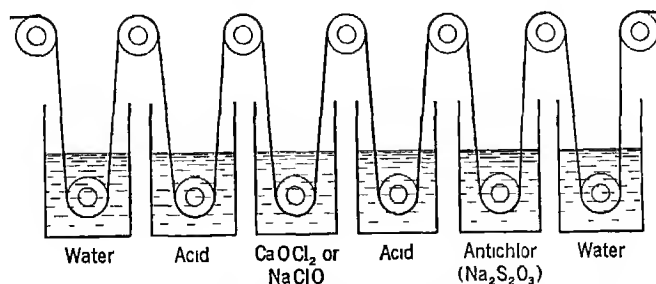
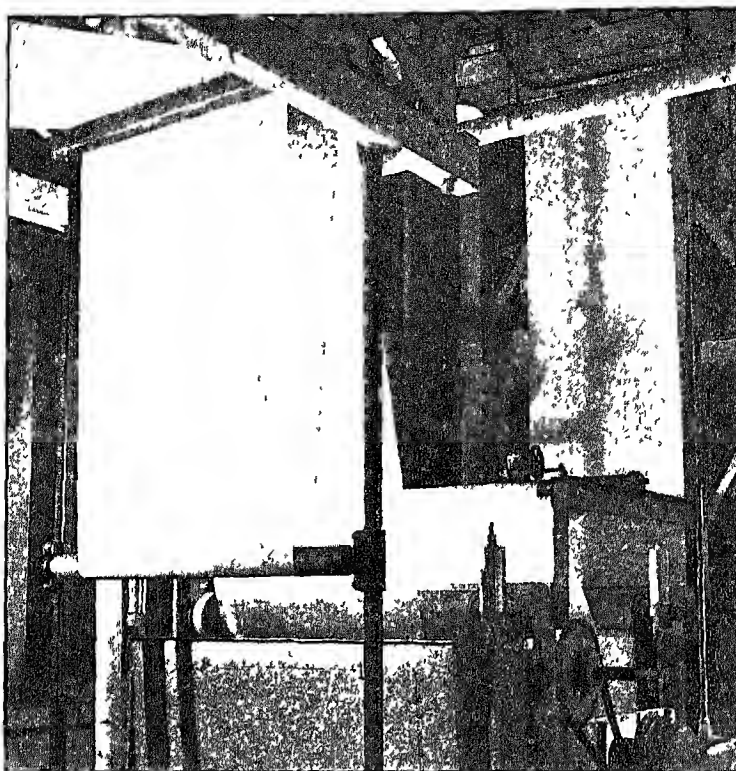


Figure 177 The Bleaching of Cloth by Means of a Solution of Sodium Hypochlorite or Bleaching Powder



Courtesy of du Pont Company

Figure 178 Bleaching Cloth

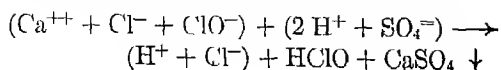
Pure white fabric emerges from the final washing operation at the end of a continuous bleaching process

methods of treatment and was the means of saving the lives of many men who otherwise would have died from the results of infection

7. Bleaching Powder

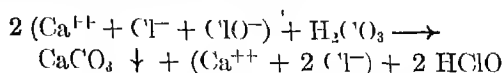
When chlorine is passed over slightly moist calcium hydroxide, a substance commonly called bleaching powder is produced. When mixed with water, this substance produces a solution containing calcium, Ca^{++} , chloride, Cl^- , and hypochlorite ion, ClO^- . It is assigned, therefore, the formula $\text{CaCl}(\text{ClO})$.

When bleaching powder is mixed with water, and the mixture is acidified with a strong acid, such as sulfuric, the ions of hydrochloric acid and molecules of hypochlorous acid are produced in the solution

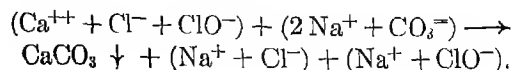


The two acids then react to liberate chlorine (page 366)

When it is exposed to the air, bleaching powder reacts with carbonic acid to liberate only hypochlorous acid, the few hydrogen ions supplied by the weak carbonic acid are used to form molecules of the weak acid HClO , and the number remaining is too small to be considered, along with chloride ions, as hydrochloric acid



Javelle water can be produced by treating a suspension of bleaching powder in water with sodium carbonate.



The calcium carbonate is only slightly soluble and can be removed by filtration, leaving a fairly pure solution of the two sodium salts. This reaction is sometimes used to produce the Javelle water used in laundries and as an antiseptic or disinfectant.

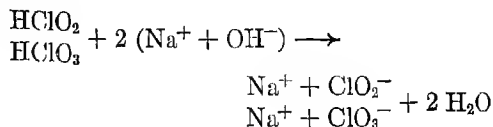
Bleaching powder is made from inexpensive raw materials, is easily manufactured, can be transported readily, and its chlorine can be liberated easily whenever required. It usually contains about 36 per cent of available chlorine. It must be transported and stored in air-tight containers to prevent its reaction with the carbon dioxide and the moisture of the air. A product called *high test hypochlorite*, or H T II, that contains almost all of its chlorine in an available form is now used for some purposes in place of ordinary bleaching powder. It is essentially calcium hypochlorite, $\text{Ca}(\text{ClO})_2$, but as it is usually sold it is mixed with slaked lime so that its available chlorine content is reduced to about 60 per cent.

Bleaching powder is sometimes called "chloride of lime," but this name cannot correctly be applied to this substance, which is as much a hypochlorite as it is a chloride.

8. Chlorous Acid and Its Salts

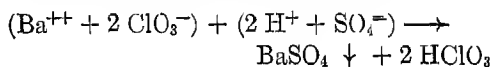
Until recently, chlorites have been of little importance. Sodium chlorite, NaClO_2 , however, is now produced and used commercially in large quantities as a bleaching agent for certain kinds of cotton cloth, rayon, and other fabrics that are weakened materially when they are bleached by a hypochlorite. Sodium chlorite is produced commercially by a series of rather complicated reactions that we shall not attempt to describe in full. Chlorine dioxide is first produced by a reaction between calcium chlorate and hydrochloric acid. The dioxide then reacts with sodium hydroxide, calcium hydroxide, and carbon. The two products are calcium carbonate, which precipitates, and sodium chlorite, which is recovered by evaporation and crystallization.

The acid exists only in solution. Chlorine dioxide reacts with water to form both chlorous and chloric acids (page 365). If sodium hydroxide is added to the solution, and the solution is evaporated, a mixture of sodium chlorate and sodium chlorite is obtained.



9. Chloric Acid and Its Salts

Chloric acid is produced, in the form of a dilute solution, when a solution of barium chlorate is treated with sulfuric acid.

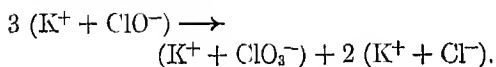


The quantity of sulfuric acid added is the exact amount required to react with the quantity of barium chlorate present. If this procedure is followed carefully, the resulting solution will not contain any excess of sulfuric acid. The barium sulfate is only slightly soluble and can be removed by filtration. The dilute solution of chloric acid can be concentrated to 40 per cent of HClO_3 , if the solution is evaporated at a lower temperature than 40°C . This is possible if the solution is heated under very low pressure or is placed in a vacuum desiccator over concentrated sulfuric acid. Chloric acid can also be prepared by moderately heating a solution of hypochlorous acid (page 366).

Chloric acid is a colorless liquid. It is more stable than hypochlorous acid, but when it is slightly heated it decomposes violently to form chlorine dioxide. It is consequently a very active oxidizing agent, but because of its unstable character the pure acid cannot be prepared for such uses. A piece of paper that is dipped into the 40 per cent solution of chloric acid ignites spontaneously. In an acidified solution of a chlorate we may assume that chloric acid is

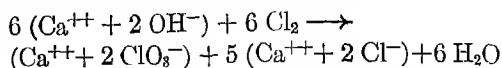
liberated temporarily and serves as the oxidizing agent

Potassium chlorate is the most important salt of the acid. It is prepared in several ways (1) It is sometimes made by passing chlorine into a hot concentrated solution of potassium hydroxide. In accordance with the reactions already discussed (page 365) chlorine reacts with water to form HCl and HClO , these acids are then neutralized by the base to form the salts KCl and KClO . The latter (KClO) is converted into potassium chloride and potassium chlorate at the elevated temperature of the solution



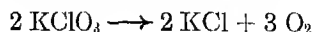
When the solution is partially evaporated and allowed to cool, crystals of potassium chlorate form and can be separated from the solution by filtering or by decantation (pouring off the clear solution from the crystals). Unless the evaporation is carried too far, the potassium chloride, which is more soluble than the potassium chlorate, remains in the solution. The potassium chlorate is purified by recrystallization. (2) A more economical process for making potassium chlorate starts with potassium chloride, which is dissolved in water and electrolyzed. The reactions that occur are the same as those in the process previously described, they are made possible by allowing the potassium hydroxide and chlorine, which are the direct products of the first reaction, to mix. The electrolysis is carried out at about 90° and between inert electrodes which are placed fairly close together so that the substances formed at the two electrodes will have a better opportunity to react. The solution, which contains potassium chlorate and potassium chloride, is withdrawn from the cell when it contains a few per cent of potassium chlorate. It is cooled to allow the potassium chlorate to crystallize, and the solution, which is separated from the crystals, is heated to the required temperature and returned to the cell. There is consequently no loss in the process.

(3) Potassium chlorate is also prepared from calcium chlorate. The latter is first prepared by passing chlorine into a moderately hot suspension of calcium hydroxide in water

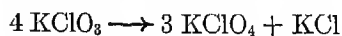


Potassium chloride is then added and reacts with the calcium chlorate to form calcium chloride and potassium chlorate; the latter, which is only slightly soluble, is recovered by crystallization, and the calcium chloride, which is very soluble, remains in the solution. The calcium chloride has little value and cannot be returned to the process to be used again, hence, all the chlorine of the potassium chloride and five sixths of that added as free chlorine is wasted.

Potassium chlorate is a white crystalline substance containing no "water of crystallization." It is sufficiently stable so that it does not decompose spontaneously at ordinary temperatures, but if it is mixed with any easily oxidized substance, such as charcoal dust, and ground to a powder in a mortar, it may explode violently. It is consequently a vigorous oxidizing agent in the dry state, when melted, and in solution. A splinter of wood or a bit of sawdust dropped into melted potassium chlorate burns very vigorously. When it is heated at moderate temperatures, slightly above its melting point, potassium chlorate decomposes into potassium chloride and oxygen



This decomposition is strongly catalyzed by manganese dioxide. If it is heated at lower temperatures and if the evolution of oxygen is avoided, potassium chlorate may be changed into potassium perchlorate



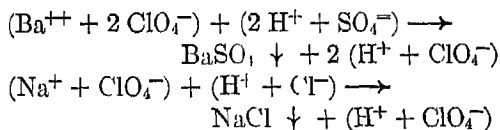
At moderate temperatures, both of these reactions proceed simultaneously and independently.

Potassium chlorate is used in the manufacture of matches and fireworks. Explosive

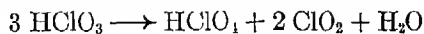
mixtures of the chlorate with easily oxidized substances, such as charcoal, sugar, or sulfur, may be prepared but are of little practical value because they are extremely unsafe, even as explosives. *Cheddite* is one explosive, however, which contains potassium chlorate. In chemical manufacturing, potassium chlorate is used as an oxidizing agent. A solution of potassium chlorate is sometimes used in treating throat infections, and it has been used in some kinds of tooth paste. Its use as a laboratory source of oxygen has already been discussed (page 67).

10. Perchloric Acid and the Perchlorates

The anhydride of perchloric acid (HClO_4) is Cl_2O_7 . A solution of the acid may be prepared by treating barium perchlorate with sulfuric acid and filtering off the insoluble barium sulfate. It may also be prepared from other perchlorates and by the action of certain other acids. If hydrogen chloride is passed through a solution that is saturated with sodium perchlorate, sodium chloride is precipitated and a solution of perchloric acid is formed.



Chloric acid, when heated, forms perchloric acid, chlorine dioxide, and water.

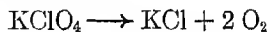


From any of these solutions perchloric acid may be obtained, in the form of a more concentrated solution, by evaporation under reduced pressure. Even the anhydrous acid may be prepared, since it is fairly stable at temperatures below 90° . The acid may be distilled at 40° , under a pressure of about 55 mm, without any decomposition. The pure acid decomposes explosively when heated very strongly and sometimes explodes spontaneously in storage. For this reason it is usually supplied and used as a 60 or 70 per cent solution. It is a strong oxidizing agent as shown by the immediate ignition of wood

or paper with which it comes in contact. It is less vigorous, however, in its oxidizing action than chloric acid. It does not oxidize hydrogen chloride in a cold solution, and it does not affect many other substances that are vigorously attacked by chloric acid. In addition to the anhydrous acid, perchloric acid is known as two hydrates called oxonium and dioxonium perchlorate, OH_3ClO_4 and $\text{O}_2\text{H}_5\text{ClO}_4$, still other less well-known and less important hydrates also exist.

Perchloric acid, in 60 per cent solution, is used in analytical procedures to detect and also to determine the quantity of potassium in samples of materials that contain this element. This use of perchloric acid is based upon the slight solubility of potassium perchlorate, as compared with the solubilities of other perchlorates and other potassium salts. Perchloric acid is one of the strongest of all acids, comparing favorably in this respect with hydrochloric and nitric acids.

Potassium perchlorate is the most important of the salts of perchloric acid. It is prepared by carefully heating potassium chlorate (page 370). It may also be prepared by the electrolysis of a solution of potassium chloride. If the solution is moderately heated, potassium chlorate is formed, and if electrolysis is allowed to proceed for a longer period of time, the chlorate is oxidized to the perchlorate. When heated strongly, potassium perchlorate acts similarly to the chlorate.

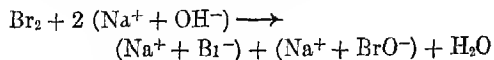


The perchlorates are active oxidizing agents but are considerably less vigorous in their action than the chlorates. Potassium perchlorate is used in the manufacture of matches, fireworks, and explosives. Anhydrous barium perchlorate and magnesium perchlorate are excellent dehydrating agents and are supplied, usually as a mixture of the two salts, for this use.

11. Oxygen Acids of Bromine and Their Salts

Two oxygen acids of bromine and their salts

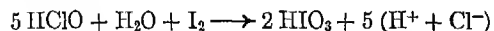
are fairly familiar substances. These are hypobromous acid (HBrO) and bromic acid (HBrO_3). Aqueous solutions of these acids and then sodium or potassium salts are prepared in the same way as the corresponding compounds of chlorine. Bromine shows less tendency than chlorine to react with water, but in the presence of a base the reaction is almost complete



The acids cannot be prepared in the pure states because of their instability. Bromic acid may be prepared in solution by the action of strong oxidizing agents, such as hypochlorous or chloric acids, upon bromine. The properties of the acids and their salts are similar to those of the corresponding compounds of chlorine. They are not much used, however, because of the relatively slight availability of bromine as compared with chlorine.

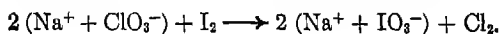
12 Oxygen Acids of Iodine and Their Salts

Although iodine reacts only slightly with water, the reaction is almost complete in the presence of sodium or potassium hydroxide. Sodium hypoiodite is first formed, but in a warm solution is quickly converted into the iodate. The reactions are of the same character as those which involve chlorine. Iodic acid can be prepared by treating iodine, suspended in water, with chlorine. The latter reacts with the water to form hypochlorous acid, which then oxidizes iodine to iodic acid



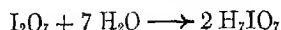
Nitric acid also oxidizes iodine to iodic acid. If the solution resulting from the oxidation of iodine is evaporated, crystals of iodic acid separate. The crystals of the acid are stable at ordinary temperatures. If heated to $175^\circ - 200^\circ$, water is expelled and the anhydride (I_2O_5) is left. In aqueous solution iodic acid is a somewhat less active oxidizing agent than chloric and bromic acids.

Sodium iodate is the most important salt of iodic acid. It is found in the deposits of sodium nitrate in South America (page 340). It may be prepared by the action of sodium chlorate upon iodine

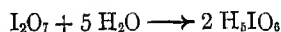


The iodates and iodic acid have limited uses as reagents in the chemical laboratory, and the former have some slight use in medicine. The anhydride of iodic acid (I_2O_5) is used in the detection of carbon monoxide.

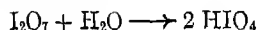
There are several acids to which the name periodic may be applied. All of these may be considered as derived from the anhydride, I_2O_7 , which the different acids combine with any number of molecules of water from one to seven. The acid formed by the reaction of I_2O_7 and seven molecules of water corresponds to what might be called the hydroxide, $\text{I}(\text{OH})_7$.



This acid and its salts are not known definitely to exist. The best-known salts are derivatives of H_5IO_6 ,



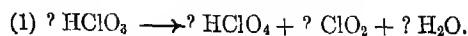
and metaperiodic acid,



Sodium periodate may be prepared by the oxidation of sodium iodate in a hot alkaline solution with chlorine. It is also found with sodium iodate in the Chilean saltpeter deposits. The free acid H_5IO_6 may be obtained as a white solid by evaporating a filtered solution in which sulfuric acid has been allowed to react with barium periodate. In acid solutions, the periodates are vigorous oxidizing agents.

13 Writing Equations Involving the Oxidation and Reduction of Oxygen-Halogen Compounds

Some of the reactions which we have discussed in this chapter are not particularly easy to balance and offer excellent material for further practice in using the methods of balancing equations which were first introduced on page 356. We shall show how these methods are applied to one of the reactions studied in the preceding paragraphs



Valence number of chlorine
in HClO_3 , 5
in HClO_4 , 7
in ClO_2 , 4

Each chlorine atom that goes into a molecule of perchloric acid must gain two units of positive

valence or lose two electrons. Each chlorine atom converted into chlorine-dioxide loses one unit of positive valence or gains one electron. To balance the equation the number of electrons lost by some of the chlorine atoms must be equal to the number gained by others; this means, of course, that a certain number of chlorine atoms must lose as much positive valence as a certain different number gains. Since each atom that gains electrons gains only one, and since each atom that loses electrons loses two, it is evident that the number of atoms gaining electrons must be twice as great as the number losing electrons. Hence, for each molecule of perchloric acid among the products of the reaction, there must be two molecules of chlorine dioxide. Three molecules of chloric acid are required to supply these three atoms of chlorine



Review Exercises

- What are the names of the following compounds? CaCl_2 , $\text{Ca}(\text{ClO})_2$, $\text{Ca}(\text{ClO}_2)_2$, CaOCl_2 , $\text{Ca}(\text{ClO}_3)_2$, $\text{Ca}(\text{ClO}_4)_2$. What is the valence number of chlorine in each of these?
- How does the stability of the oxygen-acids of chlorine, and their salts, vary with the amount of oxygen in the molecule?
- Why is it less expensive to prepare potassium perchlorate by electrolyzing a solution of potassium chloride, under the proper conditions, than it is to prepare it by heating potassium chlorate?
- What impurity would you expect to find in potassium chlorate prepared by treating a warm solution of pure potassium hydroxide with pure chlorine?
- Explain how chlorine is liberated when bleaching powder is treated with a dilute solution of sulfuric acid.
- Write equations showing all the reactions that occur when concentrated sulfuric acid is dropped upon solid potassium chlorate. Why is this reaction not used as a means of producing chlorine? (See page 365.)
- Write a balanced equation to show the oxidation of hydrogen chloride to free chlorine and water by potassium chlorate. Why is this reaction not used to produce chlorine?
- Calculate the weights of pure potassium chlorate and potassium perchlorate which would be required to produce 16 grams of oxygen when they are strongly heated (separately).
- If liquid chlorine costs five cents per pound, and bleaching powder (36 per cent of available chlorine) costs three cents per pound, which is the less expensive material to use in purifying the water of a swimming pool?
- Write equations for all of the reactions that occur when a hot solution of sodium hydroxide is treated with bromine.
- Write a balanced equation that shows the oxidation of iodine to iodic acid by nitric acid if the nitrogen appears at the end of the reaction as nitric oxide (NO).
- Make a list of the oxygen-acids of the halogens, and their sodium salts. State some of the uses of the acids or their salts.
- How would you prepare the barium chlorate which is used in making a fairly pure solution of chloric acid (page 369)?
- Write a balanced equation to show the reaction of calcium hydroxide with chlorine if the products of the reaction are water, calcium chloride, and calcium chlorate.
- What are some of the indications, as revealed by the properties of their compounds, that chlorine is more electronegative — has greater attraction for electrons — than iodine?
- What is the valence number of iodine in the acid HIO_3 ? Account for the fact that the valence number of the iodate radical IO_3^- is -1 .
- Solutions of hydriodic acid become discolored when they are allowed to stand in the light. Explain what happens.
- Show by the method explained on page 372 how the equation for the conversion of potassium chlorate to potassium perchlorate is balanced.
- Write the formulas for potassium iodate, sodium bromate, calcium periodate, the anhydride of perchloric acid, and magnesium hypobromite.
- What weight of potassium chlorate could be produced by the action of an excess of chlorine upon one liter of 10 normal potassium hydroxide solution? Assume that the product recovered amounts to 90 per cent of the theoretical yield.

21. How can potassium perchlorate be obtained in a fairly pure condition from a mixture which contains potassium perchlorate, potassium chlorate, and potassium chloride?
22. How would you bring about the following changes? (1) $\text{NaCl} \rightarrow \text{NaClO} \rightarrow \text{NaClO}_3 \rightarrow \text{NaCl}$
23. A compound contains 31.9 per cent of potassium, 39.2 per cent of oxygen, and 28.9 per cent of chlorine. What is the formula of the compound?
24. A sufficient quantity of sulfuric acid to react completely with 100 g. of barium chlorate was added to a solution containing the latter. The solution was then filtered, and the precipitate was washed and dried. Assuming complete precipitation, what did the precipitate weigh?
25. If the filtrate (of 24) contained two liters of

water, what was the percentage of chloric acid in the solution, assuming that all the chlorate ion was converted into this acid?

References for Further Reading

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- Chlorine Compounds *Chem and Met Eng*, 33, 274 (1926), *J. Chem Ed*, 4, 596 (1927); 22, 283 (1945)
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- Sodium Hypochlorite *Ind. and Eng. Chem*, 15, 845 (1923)

THE ALKALI METALS

The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface, at the lower or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic luster and being exactly similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces

DAVY, "THE DISCOVERY OF POTASSIUM"

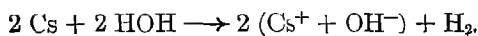
1 Introduction

Following our study of the halogens as a family of non-metallic elements we take up next a family of the metals. We select as the family to be studied the elements of the A division of group one of the periodic classification: lithium, sodium, potassium, rubidium, and cesium. Number 87, discovered by Peery in 1939 and now called *francium* (Fr), is a member of the family. These elements are usually called the *alkali metals*. This family is selected as an introduction to the study of the metals because its members display the chemical characteristics of metals, as opposed to non-metals, most prominently. We have selected this family of metals, also, because many of the compounds of two of its members (sodium and potassium) are among the most familiar and important of all substances. The compounds of lithium, rubidium, and cesium are relatively unimportant. We shall emphasize, therefore, the properties and compounds of sodium and potassium as the principal representatives of the family.

2 General Properties of the Family

The characteristic valence number of each

element of the alkali family is positive 1. This valence (page 58) depends upon the presence of a single electron in the outermost group of each kind of atom; this electron is easily transferred to electronegative elements, such as chlorine. We find that the tendency to lose this electron becomes greater as the atomic weight increases from lithium to cesium. The electron in the cesium atom is farther removed from the nucleus of the atom than the electron in the atoms of any other element in the family. In the lithium atom it is closer to the nucleus than in any of the others. In its reactions with other substances cesium, therefore, displays stronger electropositive characteristics than the other members of the family, because its atoms more readily than atoms of the other elements lose their valence electrons. All of the alkali metals react with water to form hydroxides and to liberate hydrogen, but cesium displays the greatest activity in this reaction. This means, of course, that the atoms of this element can most easily transfer their valence electrons to atoms of hydrogen, thus reducing this element.



The reaction of this metal, and also of potassium and rubidium, with water liberates enough heat to cause the metal to ignite almost instantly.

Because of their pronounced electropositive characteristics, these elements ordinarily form electrovalent (ionic) compounds. Even the hydrides, such as lithium hydride (LiH), are electrovalent in character as shown by the tendency of the metallic ion, during the electrolysis of the compound, to move toward the cathode. Consequently, hydrogen must have a negative valence number of 1 in these compounds. Covalent compounds of the alkali metals are unusual. As further evidence of the relatively weak attraction these elements have for electrons, we find that all of them are excellent conductors of electricity. This means that their valence electrons are loosely bound to their atoms and are more or less free to move from atom to atom under the influence of a difference in electrical potential (voltage).

The contrast between cesium, as the most active metal, and fluorine, as the most active non-metal, is greater than the contrast between any other pair of elements in the periodic classification. Thus, fluorine is the most vigorous oxidizing agent, and cesium is the most active reducing agent. Fluorine is the most difficult of all the elements to oxidize, in fact, it cannot be oxidized by any other element. Cesium standing at the top of the electrochemical series is very easily oxidized to cesium ion, Cs^+ , which, in turn, is difficult to reduce. The fluorine atom attracts electrons more strongly than any other atom,

cesium displays the weakest attraction, if we disregard the inert elements. To sum up these differences, we may say that fluorine atoms have the strongest tendency to acquire electrons and become negative ions, while cesium atoms most easily lose electrons and become positive ions.

All of the alkali metals are white and have a brilliant luster. They are so soft that they can be cut easily with a knife. Because of their activity, they are never found naturally in the free state. When prepared they must be stored under oil or in sealed tubes. In the air they react not only with oxygen but with water and carbon dioxide. The student who first examines these elements in a casual manner is not likely, perhaps, to associate them with elements that he knows to be metals. We usually think of metals as durable and strong substances that can be used to make tools or build more or less permanent structures. The alkali metals are not durable and they lack strength; but, judging them from their chemical behavior, they are more typically metallic in character than iron, copper, lead, gold, tin, nickel, and aluminum. This means, for example, that their oxides are the anhydrides of strong bases, that their hydroxides show no tendency (or at least almost no tendency) to react as acids (HNaO , etc.), and that their most familiar and characteristic compounds are substances in which the metals act always as positively charged ions (Na^+Cl^- , K^+NO_3^- , Cs^+Cl^- , etc.). Contrast with this behavior,

TABLE 20
Properties of the Alkali Metals *

Metal	Electron Groups	Atomic Number	Atomic Weight	Specific Gravity	Melting Point	Boiling Point	Specific Heat
Lithium	2-1	3	6.94	0.53	186°	1200°	0.837
Sodium	2-8-1	11	22.997	0.97	98°	880°	0.297
Potassium	2-8-8-1	19	39.096	0.86	62°	760°	0.192
Rubidium	2-8-18-8-1	37	85.44	1.53	38.5°	700°	0.079
Cesium	2-8-18-18-8-1	55	132.81	1.9	26°	670°	0.048

* The regular changes in the physical properties of the alkali metals with changes in atomic weight and structure are clearly shown in this table.

that of chlorine, whose oxides are the anhydrides of acids, whose hydroxide acts only as an acid ($\text{ClOH} \rightarrow \text{HClO}$), and which acts usually as a negative ion (Na^+Cl^-) or as an element in a negative radical (K^+ClO_3^-)

SODIUM AND ITS COMPOUNDS

3. History

Metallic sodium and potassium were first prepared by Sir Humphry Davy in 1807. Previous to this time, the substances that we now recognize as sodium and potassium hydroxides were regarded as elements and were called the "fixed alkalis." Davy prepared the metals by electrolyzing the fused hydroxides. He described the products as "inflammable substances very like metals."

4. Occurrence

Although free sodium does not occur in nature, several of its compounds are familiar and abundant substances. The common source of sodium compounds, and of chlorine as well, is sodium chloride (salt). The occurrence of this substance is discussed in other sections (pages 327 and 379). Large amounts of sodium are also present in certain silicate rocks of the earth, such as the sodium feldspar known as *albite* ($\text{NaAlSi}_3\text{O}_8$). During the weathering of these rocks, sodium compounds are produced in the soil resulting from the decomposition of the rocks. Plants growing upon this soil derive the sodium that they require from this source. Since all of its common compounds are readily soluble in water, most of the sodium is leached out of the soil by water and finds its way eventually into the sea. Only in arid regions of the earth, where there is little water to dissolve and carry away the sodium compounds, is it possible for significant deposits of sodium salts to form. Several deposits in desert or semi-desert regions are of great importance, not so much for the sodium that they contain, but for other constituents of the compounds found in the deposits. Deposits of sodium nitrate are found in Chile

(page 340), sodium carbonate occurs naturally, as the mineral called *trona*, in Egypt, California, and elsewhere, and borax ($\text{Na}_2\text{B}_4\text{O}_7$) is found in the Death Valley region of southern California.

5. Preparation of Metallic Sodium

Before the generation of the electrical current by means of the dynamo became a source of industrial energy, metallic sodium was produced by reducing sodium carbonate with iron. This process was difficult and somewhat dangerous. With the development of the dynamo, Davy's original method of preparing sodium came to be the industrial process for producing the metal.

Davy's method of producing metallic sodium by electrolyzing melted sodium hydroxide was widely used at one time, but all of the metal now made in America is produced by the electrolysis of fused sodium chloride. The hydroxide is preferable for one reason, it melts at a temperature (318°) approximately 500° below the melting point of the chloride. If the hydroxide is used, however, it must first be prepared from the chloride, hence it is highly desirable to eliminate this step and prepare the metal directly from the chloride. The melting point of sodium chloride is only 805° , and this temperature is not sufficiently high to offer any serious difficulty. Since electrolysis requires the use of electrical energy, plants for the production of metallic sodium usually are located where water power for the production of electricity is available.

The electrolysis of fused sodium hydroxide is carried out in the Castner cell (Figure 179). The outside vessel is made of iron. The heat required to melt the sodium hydroxide is produced by the resistance encountered by the electric current, but an additional source of heat is provided by gas burners. The sodium hydroxide in the lowest portion of the vessel remains solid and helps to support the cathode, which is an iron bar or a graphite rod. The anode consists of several bars of iron, or an iron cylinder, suspended from the top of the cell. An iron cylinder,

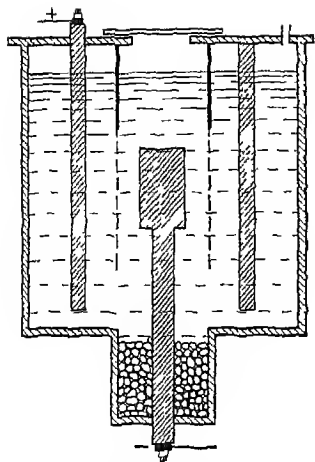


Figure 179 The Castner Cell for the Production of Metallic Sodium by the Electrolysis of Fused Sodium Hydroxide

to which is attached a non gauze, surrounds the upper end of the cathode and separates it from the anode bars. The gauze tends to keep the products which are liberated at the two electrodes separated. Sodium and hydrogen are liberated at the cathode. The sodium is in the fused state and being lighter than the fused hydroxide rises to the surface in the center. It is protected from the air by the hydrogen which escapes with it. The sodium is removed from this space in ladles as it accumulates.

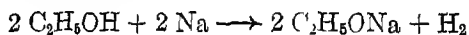
Another type of cell that is used to produce metallic sodium from sodium chloride is shown in Figure 180. The metal is liberated on the surface of the cathode and rises to the top of the cathode compartment. At the temperature at which the cell is operated, the sodium remains in the liquid state, finally overflows into the receptacle shown at the right in Figure 180, and is collected under oil. The chlorine that is liberated around the anode escapes through the opening in the top of the cell. The electrolyte used in this process is either fused sodium chloride or a mixture of fused sodium and calcium chlorides, the melting point is lowered by the addition of calcium chloride.

6 Properties of Metallic Sodium

Sodium is a very soft metal that can be cut easily with a knife and molded into any desired form. It has a brilliant silver-white appearance when freshly cut. It is slightly

lighter than water, its specific gravity is 0.97. It melts at 98° and boils at 880° . The vapor appears to consist of monatomic molecules. It dissolves in liquid ammonia to form a blue solution. The vapor, also, has a blue color, and small particles of the metal which are dispersed in rock salt impart the same color to crystals of this substance.

Chemically, sodium possesses the properties of a very active metal. It combines readily with most of the non-metals, such as oxygen, chlorine, sulfur, bromine, and iodine. With oxygen it forms the oxide Na_2O and the peroxide Na_2O_2 . When sodium burns, the latter is produced. It displaces hydrogen from most acids, forming the sodium salt of the acid. It vigorously decomposes water, liberating hydrogen and forming sodium hydroxide (page 108). It is a vigorous reducing agent, often acting violently in this respect, e.g., the reduction of hydrogen in water. It reacts with alcohol in a similar manner, displacing hydrogen and forming sodium alcoholate.



It also reduces many of the metals when it reacts with their oxides or chlorides. It forms alloys with several of the metals. Some of the more important of its alloys are sodium amalgam (an alloy with mercury).

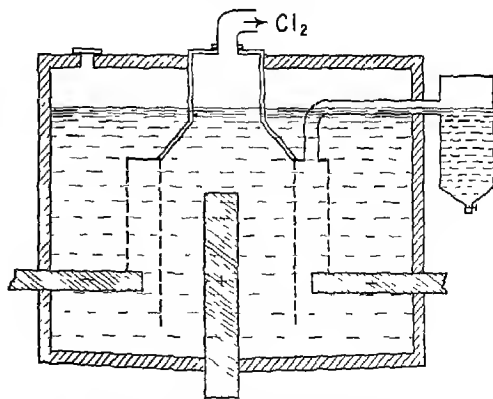
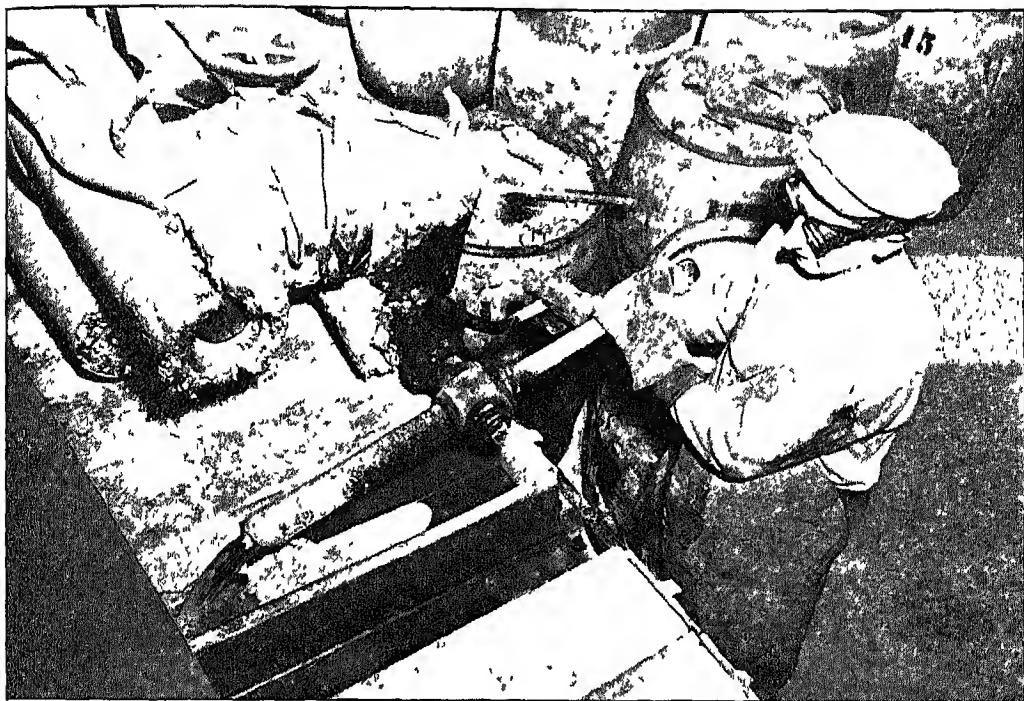


Figure 180 The Downs Cell for the Production of Metallic Sodium by the Electrolysis of Fused Sodium Chloride



Courtesy of du Pont Company

Figure 181 Casting Bricks of Metallic Sodium

hydride (an alloy with lead), and the alloy of sodium and potassium, which is a liquid at ordinary temperatures. Sodium and certain of its compounds volatilize when heated in the flame of a Bunsen burner, they impart a yellow color to the flame. When this light is examined spectroscopically (page 231), a strong yellow line is observed. This and also the yellow color of the flame itself often serve as means of identifying sodium compounds or detecting them in substances of unknown composition.

7 Uses of Metallic Sodium

Metallic sodium is used to prepare compounds of the element which cannot be prepared readily from the chloride. The most important of these are sodium peroxide and sodium cyanide. It is also used to produce compounds of other elements including lead tetraethyl (ethyl gasoline), some dyes, and other organic compounds. It has limited use as a reducing agent for the reduction of

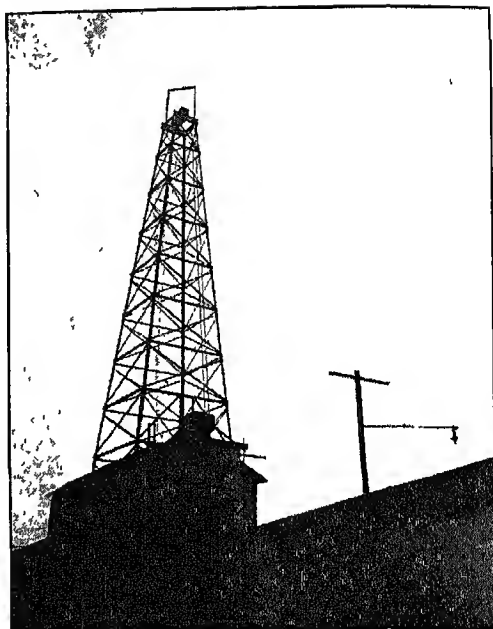
some metals from their oxides or chlorides. Thus, before the modern method of producing metallic aluminum was introduced, this metal was made by reducing aluminum chloride with metallic sodium. When a small quantity of sodium is placed in an evacuated tube and electricity is discharged through the tube, some of the sodium vaporizes. A tube of this kind containing neon, as well as sodium vapor, is now used as a lamp. Encased in non pipes, it is used as an electrical conductor. It is placed in the hollow valve stems of some airplane motors, because it is an excellent conductor of heat, and therefore aids in the prevention of overheating.

8 Sodium Chloride

The usual source of all sodium and chlorine compounds is sodium chloride. This is one of the world's most abundant mineral substances. Three per cent of the water of the oceans consists of dissolved solids, of which two thirds is sodium chloride. The water of

the Dead Sea and of Great Salt Lake contains about 20 per cent of sodium chloride. Many deposits of salt occur in different parts of the world. Usually these are deposits that have been left when the water of lakes or of isolated arms of the sea has evaporated. There are, for example, enormous deposits of salt in the Stassfurt region of Germany, and in this country there is an extensive deposit, about 400 to 500 feet thick, underlying parts of Oklahoma, Texas, and Kansas. Important deposits are also found in New York, Michigan, California, Louisiana, West Virginia, and Ohio. These beds lie beneath the surface, and the salt is removed either by mining or by forcing water down into the deposits to form strong brines, which are then pumped to the surface through wells. The production of salt in the United States amounts to more than 9,000,000 tons per year. Most of this comes from deposits and very little from sea water. Salt is purified by dissolving the crystals in water, concentrating the solution, and allowing the crystals to form again. Most of the common impurities of salt are more soluble and remain in solution when the salt crystallizes. Salt usually contains a little magnesium chloride, which is hygroscopic and tends to cause the salt to "cake." Salt grains in this condition will not "pour," but clog the openings in the "salt-shaker." To prevent caking, starch may be added to coat each grain of salt, or sodium bicarbonate may be added to convert the magnesium chloride into the carbonate which is not hygroscopic.

Sodium chloride is an essential constituent of foods. In addition to making food more palatable, it is the source of chlorine from which the hydrochloric acid found in the gastric juice is produced. Sodium chloride is also found in the blood. A physiological salt solution, containing about 0.8 per cent of sodium chloride, is sometimes used, as an injection in treating persons who have suffered considerable loss of blood. Sodium chloride is also used as a preservative of foods, and in producing freezing mixtures



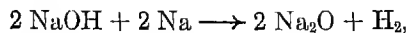
Courtesy of Pittsburgh Plate Glass Company

Figure 182 A Salt Well

(page 209). The most extensive use of salt, however, is in the manufacture of chlorine, hydrochloric acid, sodium hydroxide, sodium carbonate, and other compounds of sodium and chlorine. Very pure sodium chloride may be prepared by passing hydrogen chloride into a saturated solution of salt.

Oxides of Sodium

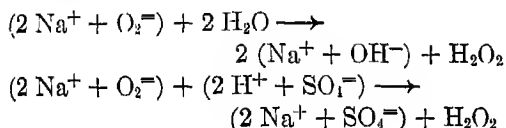
Sodium forms two oxides, Na_2O and Na_2O_2 . The former is a normal oxide, and the latter is a peroxide (page 186). The oxide, Na_2O , can be formed by heating the hydroxide with sodium.



or by passing oxygen over metallic sodium under very carefully controlled conditions. Until recently, it has been of little importance, but it is now used as a very effective drying agent for many kinds of materials. The peroxide is formed by the direct combination of sodium and oxygen. Chips of sodium are placed on aluminum trays which are moved slowly through a furnace (400°).

A current of air is passed into the furnace and over the trays from the other end. This is an example of the *counter current principle*, which is often used in chemical manufacturing, sodium passes one way and air the other. This method is advantageous in the manufacture of sodium peroxide because it allows fresh metallic sodium to react first with air from which most of the oxygen has been removed. As the trays pass through the furnace, the sodium comes in contact with air containing more and more oxygen, until at the time it emerges it is acted upon by fresh air. This allows the oxidation to proceed more slowly and under better control than would be possible if sodium were simply heated in the air.

Sodium peroxide is a very vigorous oxidizing agent. It reacts with water and acids to form hydrogen peroxide:



In the presence of limited quantities of water, the hydrogen peroxide produced in these reactions, and especially in the first reaction, decomposes into water and oxygen.

SODIUM CARBONATE

The most important compound of sodium is sodium carbonate. In fact, this substance rivals sulfuric acid in commercial importance. At one time, it was obtained either from natural deposits of the substance called *trona*, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2 \text{H}_2\text{O}$, or by leaching the ashes of seaweeds with water. The name "soda ash" is derived from this source of sodium carbonate. Enormous deposits of trona are located in East Africa and southern California. Most of the carbonate used in European countries at one time came from Egypt. At the present time most of the sodium carbonate used in the world is made from sodium chloride. The United States produces approximately 3,000,000 tons annually.

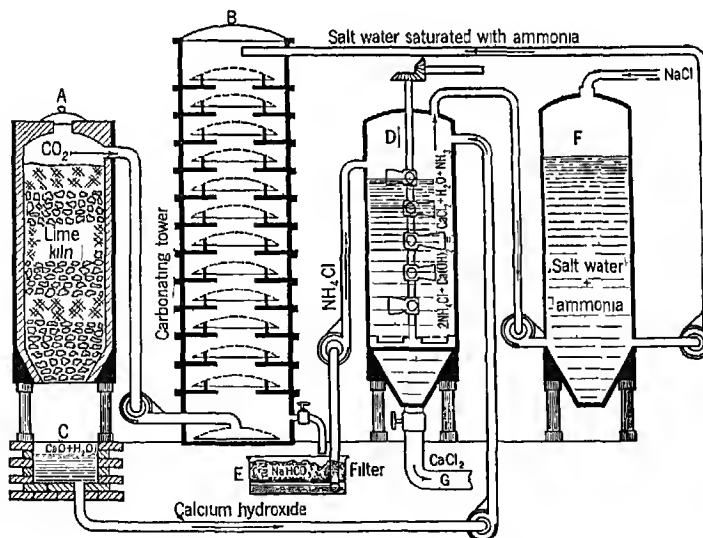


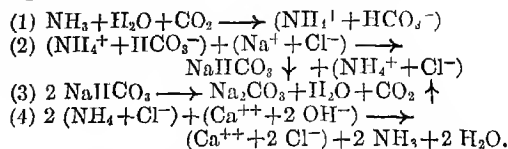
Figure 183 The Solvay Process for the Manufacture of Sodium Bicarbonate

A, lime kiln; B, carbonating tower in which sodium bicarbonate is made, C, hydrotor, where "slaked lime" is produced, D, ammonia recovery unit, where the liquor from the filter E is treated with slaked lime from C, thus liberating the ammonia from ammonium chloride, F, tank in which the ammonia recovered in D is passed into brine, the resulting solution is then pumped to B where it is used in making sodium bicarbonate.

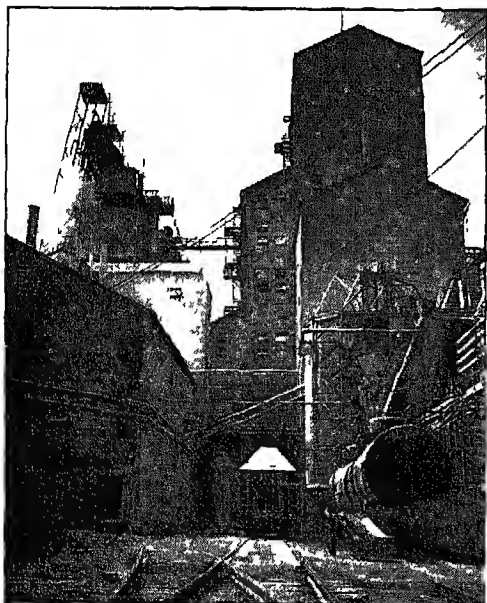
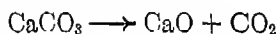
10. The Solvay Process

Most of the sodium carbonate produced in this country is manufactured by the Solvay process, which was introduced in 1860 by Ernest Solvay, a chemical engineer of Belgium. Ammonia and an excess of carbon dioxide are passed into a solution saturated with salt. The first two substances react (1) to form ammonium bicarbonate, which reacts in turn with sodium chloride (2) to form sodium bicarbonate. This substance is only slightly soluble in the salt solution, hence it precipitates and can be removed by filtration. It is purified by dissolving the crystals in fresh portions of water and evaporating the water until the bicarbonate, as the least soluble substance in the solution, crystallizes. By repeating this process several times a very pure product may be obtained. The bicarbonate may be changed (3) into the normal carbonate by heating. After the first separation of sodium bicarbonate crystals from the solution, the "mother liquor" contains ammonium chloride. Because of the ammonia that it contains, this substance is too valuable to throw

away. Hence, the "mother liquor" is treated (4) with lime, which reacts with water to form calcium hydroxide, and this product reacts, in turn, with ammonium chloride to form ammonium hydroxide. The mixture is heated to drive out the ammonia, which is then used again in the first step of the process. The reactions involved in the four steps are shown by the following equations:

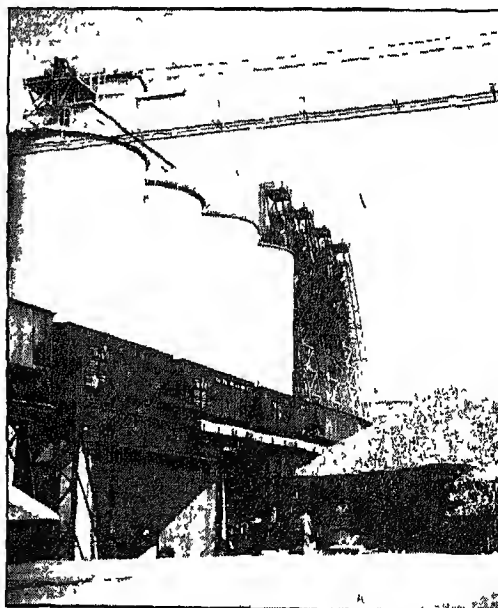


Some of the details of the plant in which sodium bicarbonate is made by the Solvay process are shown in Figure 183. The plant must be located near a salt deposit and preferably near a supply of coal. In addition to the ammonia which is recovered and returned to the process, ammonia is obtained as a by-product in the coking of coal. The lime used in step (4) is produced by the calcination of limestone:



Courtesy of Pittsburgh Plate Glass Company

Figure 184 Stills and Towers of the Solvay or Lime Soda Process for Manufacturing Sodium Carbonate



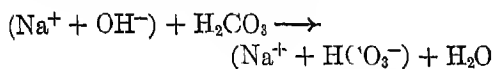
Courtesy of Pittsburgh Plate Glass Company

Figure 185 Soda Ash Storage Silos and Piles of Limestone Used in Production of Sodium Carbonate

The carbon dioxide which is produced in this reaction is used in the first step. The only by-product of the Solvay process is calcium chloride, which is not an extremely valuable substance. It may be recovered, however, and when dried, it finds use as a drying agent because of its tendency to combine with water to form the hydrate. This substance is also used to keep down dust on rock roads (a use that depends upon its deliquescence), and in treating the surfaces of new cement roads.

11. The Electrolytic Process

In the electrolytic process, sodium bicarbonate is produced by electrolyzing a solution of sodium chloride which is saturated with carbon dioxide. Sodium hydroxide is the direct product of the electrolysis (page 329), but this substance is converted into the bicarbonate by carbonic acid



If a smaller quantity of carbon dioxide is used, the normal carbonate may be prepared. Chlorine and hydrogen escape from the anode and cathode, respectively, as when a solution of salt is electrolyzed without the addition of carbon dioxide. The carbon dioxide required in the process is produced by heating limestone. The lime which is formed at the same time finds many uses. It may be allowed to react with chlorine, which is another by-product, to form bleaching powder.

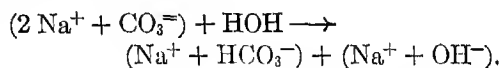
The electrolytic process has certain advantages over the Solvay process. The raw materials, salt, water, and limestone, are very inexpensive, while several valuable by-products are formed: bleaching powder, chlorine, hydrogen, lime. The process is also simple, direct, and does not require much labor. It yields a product which is easily purified. The electrolytic process is not used as generally as one would expect, however, because it requires electricity which is expensive except in places such as Niagara

Falls where water power is converted into electrical power at relatively low cost. The electrolytic process is also somewhat objectionable because the production of sodium bicarbonate on a large scale would necessitate the use of many small units instead of one, as in the Solvay process.

12. Properties and Uses of Sodium Carbonate

Sodium carbonate crystallizes from solutions in the form of large transparent monoclinic crystals of the decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$. This hydrate has a high aqueous vapor pressure, when exposed to the atmosphere, it changes to the monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. When the decahydrate is heated, it changes into the heptahydrate, $\text{Na}_2\text{CO}_3 \cdot 7 \text{H}_2\text{O}$, at 32° (the transition point). The transition point to the monohydrate is 35.4° . At higher temperatures, or in a current of dry, warm air, all the water is lost, and anhydrous sodium carbonate, commonly called soda ash, results.

The decahydrate is called *washing soda* and *sal soda*. As such, it is used in many ways as a cleansing agent. Some of the cheaper soaps contain sodium carbonate as a filler. Some soap powders contain powdered soap mixed with sodium carbonate. Sodium carbonate shows a pronounced alkaline reaction in aqueous solution. This effect is due to a reaction of sodium carbonate with water.



This is an example of *hydrolysis* (page 181). At 25°C , about 2.5 per cent of the sodium carbonate is hydrolyzed in a 0.1 N solution. Because of the basic properties of its aqueous solution, sodium carbonate is often used both in the laboratory and in industrial practice as a base. More than 30 per cent of the sodium carbonate manufactured in the United States is used in the manufacture of glass (page 384) and sodium hydroxide (page 385). Other uses include the manufacture of soaps and cleaning mixtures, many

chemicals, paper, and petroleum products. It is also used as a water softener. The more important uses of sodium carbonate and the amount (in tons) required annually in the United States for each use are shown in Table 21. The annual production in this country is about 3,000,000 tons.

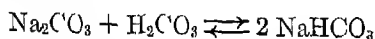
TABLE 21
Uses of Sodium Carbonate *

Glass Manufacture	860,000
Soap Manufacture	200,000
Chemical Manufacture	1,400,000
Cleaning Powders	140,000
Paper Manufacture	100,000
Water Softening	40,000
Textile Manufacture	50,000
Petroleum Products	100,000
Miscellaneous	110,000

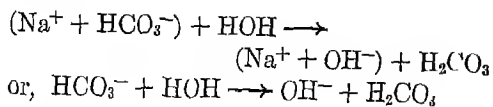
* Number of tons approximate only

13. Properties and Uses of Sodium Bicarbonate, Baking Powders

Sodium bicarbonate is produced directly by the Solvay process, by treating a saturated solution of the normal carbonate with carbon dioxide, or by passing carbon dioxide over crystals of the decahydrate of sodium carbonate.

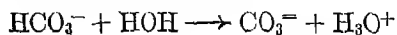


This reaction is reversible, and when moderately heated, the bicarbonate is easily converted into the carbonate. The aqueous solution of pure sodium bicarbonate is faintly alkaline because of the reaction of bicarbonate ion, as a base, with a molecule of water.



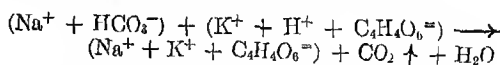
The bicarbonate is less hydrolyzed than the normal carbonate. A solution of sodium bicarbonate is sometimes used as a mild alkali, because of the hydroxyl ions liberated in this reaction, and because acids react with the bicarbonate ion to form carbonic

acid. The bicarbonate ion also possesses the properties of a weak acid, in an aqueous solution, for example, it reacts to a slight extent with molecules of water to form carbonate and hydronium ions.

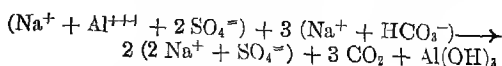


The hydronium ion thus formed is available, therefore, to react with bases. The action of the bicarbonate ion as a base is stronger than its action as an acid, hence its aqueous solution contains more hydroxyl than hydrogen (or hydronium) ions and is slightly alkaline.

The principal use of sodium bicarbonate is as an aerating agent in baking. It is sometimes called *baking soda* for this reason. The aerating action depends upon the liberation of carbon dioxide when sodium bicarbonate reacts with an acid. The acid may be supplied by using sour milk, which contains lactic acid. Baking powders contain sodium bicarbonate and some substance which acts as an acid. In aqueous solution, the acid reacts with the sodium bicarbonate to liberate carbon dioxide. The substances used as the acid in baking powder include cream of tartar, which is the acid potassium salt of tartaric acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$), and monocalcium (acid) phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Cream of tartar, for example, reacts as follows when the baking powder is mixed with water.



The so-called "alum" baking powders contain anhydrous sodium aluminum sulfate, $\text{NaAl}(\text{SO}_4)_2$. The hydrolysis of the aluminum sulfate portion of this compound produces sulfuric acid which reacts with sodium bicarbonate. Leaving out the step involving hydrolysis, the equation may be written as



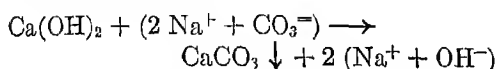
In some baking powders, mixtures of sodium bicarbonate with two or more acid substances are used. Starch or flour is added to

dilute the active components of the baking powder and to keep the material dry until it is ready for use

14. Sodium Hydroxide

Sodium hydroxide is one of the most important compounds of sodium. It is often called *caustic soda*, and its solution is called *soda lye*. It is prepared industrially by two general methods

(1) *Reaction of Sodium Carbonate and Calcium Hydroxide* A suspension of calcium hydroxide in water is mixed with a solution of sodium carbonate



This is the oldest method of manufacturing sodium hydroxide, and it is still used. It is cheaper in operating cost than the electrolytic methods but does not produce any by-products that are valuable. The calcium carbonate, which is only slightly soluble, is removed by filtration. The filtrate is evaporated to dryness, and the residue is fused to remove all the water. The melted sodium hydroxide may be molded in the form of sticks or pellets, or thin sheets of the solid may be broken up to form flakes. The sticks, the pellets, and the flakes are the usual forms in which "caustic soda" is available on the market

(2) *Electrolysis of Sodium Chloride Solutions* The production of sodium hydroxide by the electrolysis of an aqueous solution of sodium chloride has now come into general use and is the principal industrial method. One of the cells used for this purpose has been described in the chapter on chlorine (page 330). Several other cells, which operate on the same general principle, have been developed

The sodium hydroxide that is produced electrolytically contains sodium chloride as an impurity, since the chloride is not completely decomposed by electrolysis. The chloride is much less soluble than the hydroxide and crystallizes as the solution that

results from the electrolysis is evaporated. The solution may be evaporated until almost all of the chloride has separated without losing any of the hydroxide, since the latter is extremely soluble. After the removal of the sodium chloride, the solution is then evaporated completely to recover the hydroxide in the solid form. It still contains some chloride. If very pure sodium hydroxide is desired, it may be prepared by dissolving the solid in alcohol, in which sodium chloride and other impurities are only very slightly soluble. The clear solution is separated from the undissolved substances and is evaporated to produce the solid hydroxide once more. Pure sodium hydroxide may be prepared, also, by the action of metallic sodium upon distilled water.

The Castner-Kellner cell uses a mercury cathode. The sodium that is liberated at this electrode forms a dilute amalgam with the mercury and this in turn, reacts with water to form a dilute solution of sodium hydroxide. The cell is constructed according to an ingenious design and gives a very pure product. Details of its operation are shown and explained in Figure 186.

15 Properties of Sodium Hydroxide

Sodium hydroxide is a white crystalline solid. It is extremely deliquescent and is

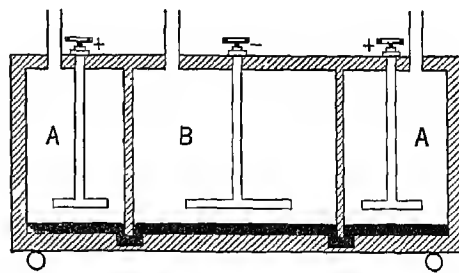


Figure 186 The Castner-Kellner Cell for the Production of Sodium Hydroxide

A, anode compartments; B, cathode compartment. The whole cell racks back and forth and the mercury, which connects the three compartments, flows first toward one end of the cell and then toward the other. In the anode compartments, the mercury acts as the cathode and forms sodium amalgam with the sodium as it is liberated. When this amalgam passes through the cathode compartment, the sodium leaves it, passing into the solution to form sodium hydroxide.

very soluble in water. It acts corrosively as its common name, "caustic soda," implies, it readily disintegrates almost all animal and vegetable tissues. In the air, sodium hydroxide absorbs water and carbon dioxide and by the latter is converted into sodium carbonate. In using sodium hydroxide or its aqueous solution in the laboratory, the most troublesome impurity is likely to be sodium carbonate. When pure sodium hydroxide solutions are desired, it is important that they should be stored under conditions which will exclude air. A glass vessel in which a solution of sodium hydroxide is stored soon becomes badly etched because of the reaction of the base with the silicates of which glass is composed. Solutions of sodium hydroxide cause one's fingers to have a "soapy" feeling when rubbed together after having been moistened with the solution. It is useful in cleaning because it reacts with grease to form soluble sodium compounds. The properties of its solution are those which characterize a strong base (page 158). Because it contains one hy-

droxyl ion in its formula, it may be called a *monacid* base; each gram-molecular (or formula) weight reacts with one gram-molecular weight of a monobasic acid, such as HCl. Calcium hydroxide is a *diacid* base.

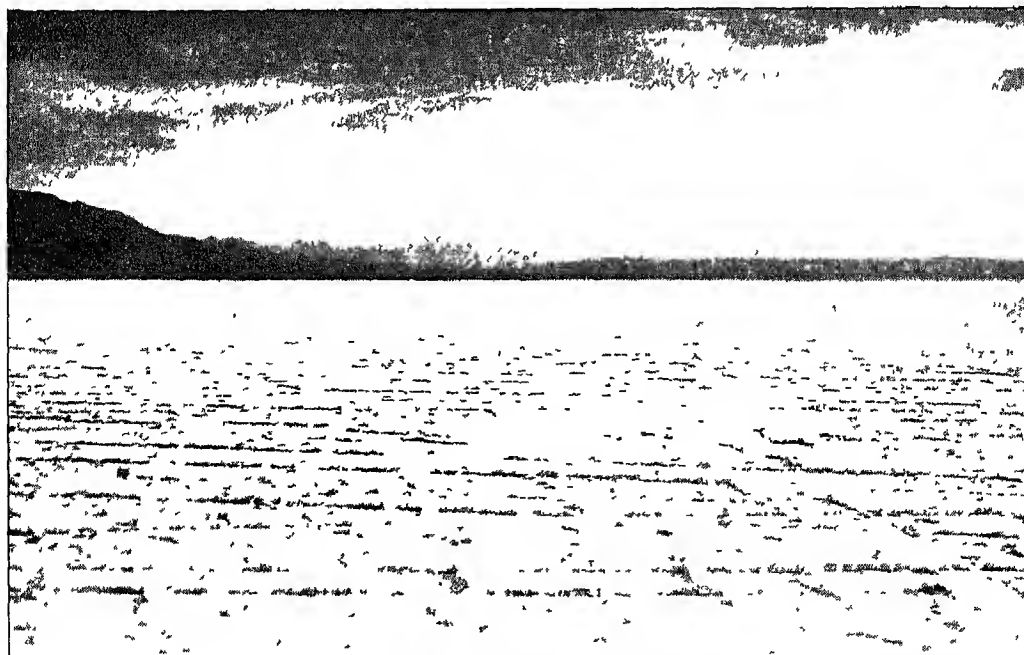
About 1,250,000 tons of sodium hydroxide are produced in the United States each year. The uses of sodium hydroxide, and the relative amounts of the substance that each use requires per year, are shown in Table 22.

TABLE 22

Uses of Sodium Hydroxide *

Soap	160,000 tons
Petroleum (purification)	150,000
Chemical Manufactures	230,000
Rayon (artificial silk)	280,000
Textiles (mercerized cotton, etc.)	65,000
Lye	75,000
Paper	65,000
Rubber (reclaiming old rubber)	15,000
Purification of Vegetable Oils	25,000
Miscellaneous	150,000

* Number of tons approximate only



Courtesy of American Potash and Chemical Corporation

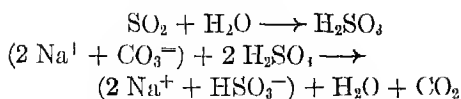
Figure 187. A View of Searles Lake

16 Sodium Sulfate (Na_2SO_4)

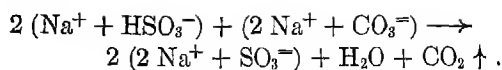
Sodium sulfate occurs naturally in deposits located in Canada and in the southwestern portion of the United States. It is also present in several mineral waters and in the water of certain lakes in Siberia. It is produced as a by-product in the manufacture of hydrochloric acid. It crystallizes from solutions at temperatures below 32.4° as the decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$. This hydrate is called Glauber's salt, after the alchemist Glauber, who used the salt as a medicine in the seventeenth century. The anhydrous salt may be formed by evaporating a solution of the substance at temperatures above 32.4° , the transition point. The hydrate also loses moisture to the air, at ordinary temperatures, because of its high aqueous vapor pressure. The transition point is so definite that it may be used in checking the accuracy of thermometers. Sodium sulfate is used to the extent of almost 400,000 tons annually in the United States in manufacturing glass and paper. In the manufacture of cheap glass, it serves as a substitute for sodium carbonate. In paper making, it is used in the preparation of wood pulp from southern pine and certain other woods. The acid sulfate (NaHSO_4) is not very useful, except in the manufacture of hydrochloric acid from salt (page 345).

17. Sodium Sulfite (Na_2SO_3) and Bisulfite (NaHSO_3)

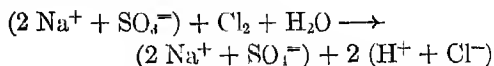
When sulfur dioxide is passed into a solution of sodium carbonate, it first reacts with water to form sulfurous acid, H_2SO_3 , which then reacts with sodium carbonate to form the acid sulfite (bisulfite)



If the saturated solution of the bisulfite is then treated with a fresh solution containing the same quantity of sodium carbonate that was used in making the bisulfite, the normal sulfite is formed



Both the normal and the acid sulfite are reducing agents. They are used to some extent as bleaching agents, as preservatives, and in photography. Sodium sulfite is used to remove the excess of chlorine when the latter is employed as a bleaching agent in the textile industry. When used for this purpose, the sulfite is called an *antichlor*. It reacts with the excess of chlorine according to the following reaction

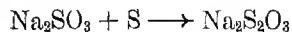


The bisulfite is used in making paper, in tanning leather, in manufacturing some dyes, and as an antichlor.

18 Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$)

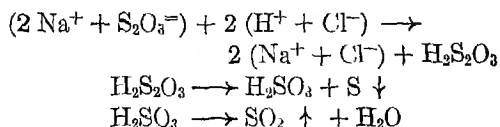
This is the substance which is familiar to photographers as "hypo." Its use in photography depends upon its ability to dissolve silver salts from plates, films, or printing paper after these have been developed. The developing process reduces the silver salt that has been effected by light to metallic silver. In the "fixing" bath, which consists of a solution of sodium thiosulfate, the undeveloped silver salts are removed so that they will not be converted into metallic silver when the "negative" or "positive" is exposed to the light.

Sodium thiosulfate is formed by treating a boiling solution of sodium sulfite with sulfur.

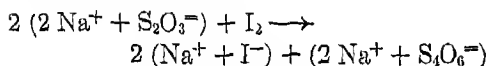


When the resulting solution is evaporated, the thiosulfate crystallizes out as the pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$. This is the substance commonly called "hypo" or hyposulfite of soda. The name hyposulfite is erroneous, however, since the substance is really a sulfate. Sulfur is oxidized in the reaction which produces the thiosulfate from a valence of 4 in Na_2SO_3 to a valence of 6 in $\text{Na}_2\text{S}_2\text{O}_3$. We may think of the second

sulfur atom as taking the place of the fourth oxygen atom in Na_2SO_4 . When an acid is added to a solution of the thiosulfate, the free acid, thiosulfuric, is liberated and, being unstable, immediately decomposes into free sulfur and sulphurous acid, which is also unstable



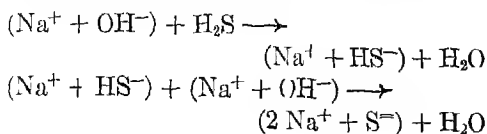
A solution of sodium thiosulfate is used to determine the quantity of iodine in materials containing iodine or iodides. If the iodine is combined, it must first be liberated by the action of chlorine or some other oxidizing agent. The free iodine then reacts with the thiosulfate as follows:



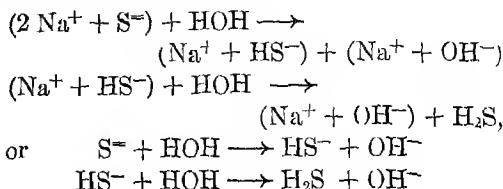
Since both sodium iodide and sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$) are colorless compounds, the addition of the required amount of thiosulfate is indicated when the color of the iodine solution disappears, or when the solution no longer shows the characteristic effect of free iodine upon starch. From the quantity of sodium thiosulfate added, the quantity of iodine present can be determined by means of the weight relations of the two substances as expressed in the equation for their reaction

19 Sodium Sulfide (Na_2S)

This compound of sodium may be prepared by treating a solution of sodium hydroxide with hydrogen sulfide. Sodium hydrosulfide (NaHS) is first formed, but if the solution is then mixed with a volume of fresh sodium hydroxide solution equal to the volume which was first saturated with hydrogen sulfide, normal sodium sulfide may be produced



Commercially, sodium sulfide may be produced by reducing sodium sulfate with carbon at a temperature of about 900° . It is a white crystalline solid which is very soluble. Its aqueous solutions are strongly alkaline in reaction because of the tendency of the salt to hydrolyze



It is used in dyeing cotton with the "sulfur dyes," in manufacturing some dyes, and in removing hair from hides in the preparation of leather.

20 Other Compounds of Sodium

The list of sodium compounds is a long one and contains many widely used and important substances in addition to those which we have already discussed in this chapter. These have been discussed previously or will be discussed later in chapters dealing with other elements that they contain. The list below will serve to designate those of major importance

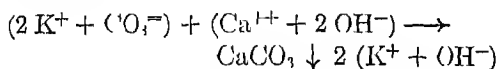
Sodium bromide and iodide	Sodium cyanide
Sodium tetraborate (borax)	Sodium phosphates
Sodium nitrate	Sodium nitrite
Sodium hypochlorite	Sodium chlorate and perchlorate
Sodium silicate	

POTASSIUM

21 Occurrence

Potassium occurs in igneous rocks in the form of micas and feldspars, of which *leucite*, KAlSi_3O_6 , and *orthoclase*, KAlSi_3O_8 , are typical. The weathering of these rocks leaves in the soil as salts at least a portion of the potassium that they contain. The salts add to the fertility of the soil, since potassium is required by plants for normal, healthy growth. After a soil has been cultivated for several years, it is likely to become deficient in potassium, which must then be added in the form of fertilizers that contain potassium salts and, frequently, salts containing nitrogen, phosphorus, and other elements.

When plants remove potassium salts from the soil, they convert them into potassium salts of organic acids. If wood and other plant materials are burned, these salts are changed into potassium carbonate, which is found in the ashes. This was the first source of potassium compounds; the ashes were leached with water, and the solution containing potassium carbonate was evaporated in iron pots to form a residue called *polash*. It was from this material that Sir Humphry Davy first produced the element. If the solution that leaches through wood ashes is allowed to flow through a bed of slaked lime, the carbonate is converted into potassium hydroxide.



The solution of potassium hydroxide is sometimes called *lye* or *potash lye*, in order to distinguish it from soda lye, which is sodium hydroxide. In pioneer days potassium carbonate or potassium hydroxide, obtained in this manner, was used to make soap. Accumulations of fat were heated with a solution obtained by leaching ashes, and a soft soap was thus produced. Wood ashes still serve to a limited extent as a source of potassium compounds.

Until recently, most of our supply of potash came from Germany, which produced most of the supply for all the world from potassium salts found in the *Stassfurt deposits* located in the north central portion of Germany. The Stassfurt deposits, like many others, were probably produced when the water evaporated in an arm of the sea that had been cut off from the main body of water by geological changes. The deposit contains about thirty different minerals (Figure 188). The lowest layer is composed chiefly of sodium chloride, which was deposited first as the water evaporated, partly because it is the most abundant salt in sea water and also because it is not so soluble as most of the other dissolved salts. The next layer contains calcium sulfate, the next, magnesium

sulfate, and the top layers contain potassium and magnesium chlorides. The most important potassium minerals among these salts are

Sylvite, KCl

Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

Kainite, $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$

Schönite, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$

Polyhalite, $\text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$

The deposit is covered with a layer of sandstone, and the different layers of salts are mixed with sedimentary material. The salts are mined, and the potassium is obtained in a more concentrated form by a very tedious and carefully controlled process in which the various salts are fractionally crystallized. The substance placed upon the market is largely potassium chloride or potassium sulfate. About 90 per cent of the total product is used in the fertilizer industry. In 1937, Germany produced about 1,500,000 tons (metric) of this material calculated in terms of its potassium oxide (K_2O) equivalency. From deposits of a similar character in Alsace-Lorraine, France produced about 490,000 tons. The United States produced about 875,000 tons of potash (calculated as K_2O) in 1945.

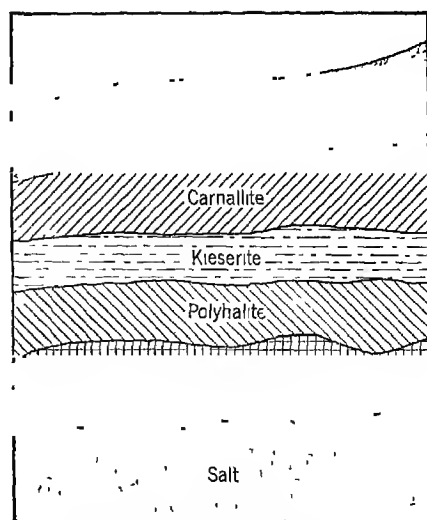


Figure 188 The Stassfurt Deposits

Prior to the first World War Germany had an almost complete monopoly on the world's supply of potash. When the United States was cut off from this source of supply, we had to look to domestic sources for the potash we needed. The price immediately soared to several times the normal cost of "potash," and this condition further stimulated the search for supplies within the boundaries of the United States. Some was extracted from *wood ashes*, but this source could not possibly supply the enormous quantity required. The feldspars, although abundant, could not be used because they are very stable substances and the cost of extracting the potassium as soluble and useful salts was prohibitive. Some was extracted from the mineral *alumite*, which is a hydrate of potassium aluminum sulfate and is found in Utah and Nevada. Some was also produced from *greensand*.

Searles Lake, in the Mohave Desert of southern California, now serves as an important domestic source of potassium salts. This is in fact not a lake, but a bed of salts about 12 square miles in area, containing salt deposits which are about 70 feet thick. The salts are present with a "mother liquor" from which they have crystallized. From this liquor and the crystallized salts, potassium chloride is produced, along with borax ($\text{Na}_2\text{B}_4\text{O}_7$) and other substances, by fractional crystallization. At one time, considerable "potash" was recovered from the ashes of kelp, from beet-sugar residues, from the ash of cottonseed hulls, the ash of wastes remaining after the fermentation of molasses, and from the dust of cement mills and blast furnaces. Since about 1931, potassium salts have been extracted from a deposit, located in New Mexico and Texas, that contains sylvite, carnallite, polyhalite, and langbeinite, K_2SO_4 , MgSO_4 . The present center of production is near Carlsbad, New Mexico. It is said that this deposit alone can supply all this country's future needs for potassium. It underlies some 30,000 square miles at a depth of 1000–1700 feet below the surface, and probably was formed by the evaporation of sea water in an arm of the sea that was cut off in the earlier geological eras of this continent. An enormous deposit of similar character was discovered in Russia in 1926.

Most of the potash now produced in the United States comes from Searles Lake and

Carlsbad, and from the fermentation industry. We have sufficient capacity for production — in 1945 this was more than 800,000 tons — to meet all our requirements. As was true for the dye and drug industries, the first World War led to the development of an American potash industry, and foreign producers lost their best market.

22. Production and Properties of Metallic Potassium

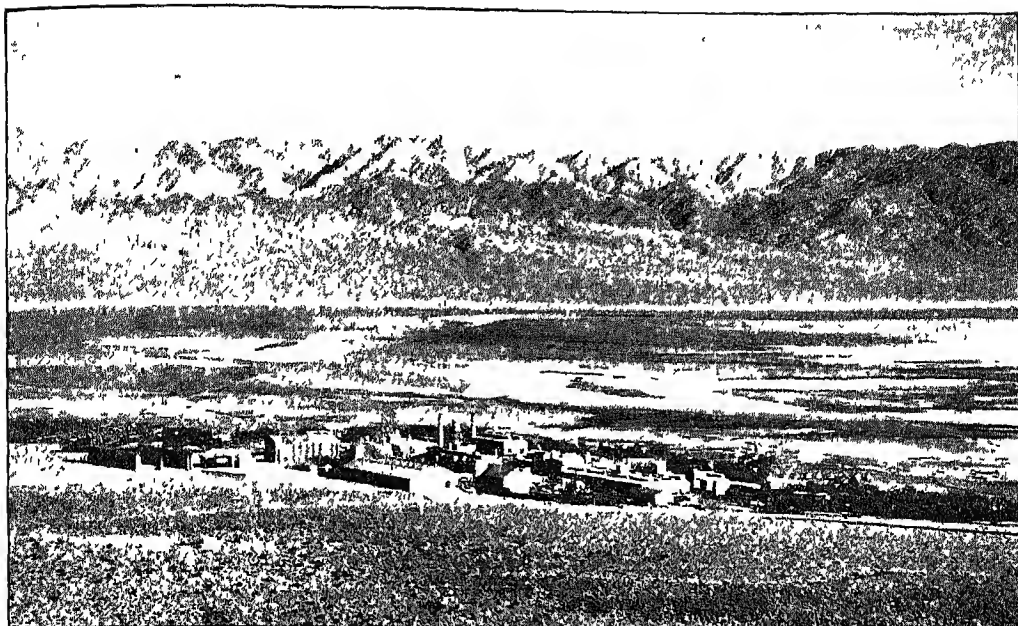
Metallic potassium is produced by the electrolysis of melted potassium hydroxide or potassium chloride, the method is the same, in general, as that used to produce sodium (page 377). Potassium can also be produced, though on a limited scale, by heating potassium hydroxide with a reducing mixture containing carbon and the carbide of iron.

Sodium is more easily and cheaply produced than potassium, and since there are no major uses for which sodium cannot serve as well, the production of potassium is limited.

Potassium resembles sodium. It is a soft metal and can be cut easily. The freshly cut surface has a bright, silvery-white luster, which is soon lost in the air, because the metal quickly reacts with oxygen and water. The metal reacts even more vigorously with water than sodium, and sufficient heat is liberated to ignite the hydrogen that it displaces.

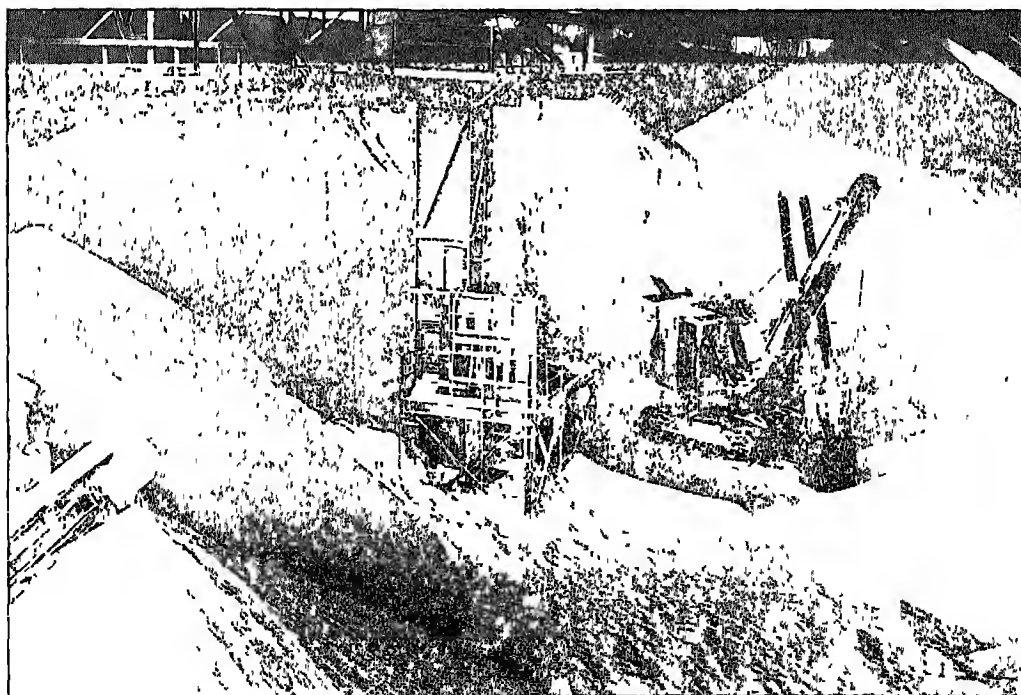
Potassium stands above sodium in the electrochemical series. The valence electron of the potassium atom is more easily removed than the valence electron of the sodium atom, as we should expect, since the former lies in a group farther removed from the nucleus than the latter. For the same reason, the potassium ion is not so easily converted into an atom of the metal as the sodium ion.

Metallic potassium boils at 760° , and the greenish colored vapor appears, from its density, to consist of monatomic molecules. When the metal and its compounds are heated in the flame of a Bunsen burner, they



Courtesy of American Potash and Chemical Corporation

Figure 189. Searles Lake



Courtesy of American Potash and Chemical Corporation

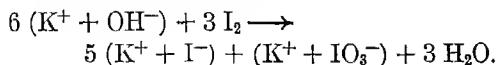
Figure 190 Potash Storage and Loading Equipment

impart to it a violet color. The color of this flame is observed best through a piece of cobalt (blue) glass, which absorbs all the colors of light from the flame except the blue and violet.

23 Potassium Halides

Most potassium compounds are made from potassium chloride. This substance is obtained chiefly from sylvite and carnallite (page 389). It is purified by dissolving these minerals in water and fractionally crystallizing the salts that they contain. In carnallite, potassium chloride is present with magnesium chloride, which is much more soluble and hence remains in solution as the potassium chloride crystallizes. The separation from sodium chloride is fairly easy, since this impurity is less soluble than potassium chloride at temperatures above 30°, and its solubility changes but little between this temperature and 100°. Potassium chloride, on the other hand, shows a greater range of solubility at different temperatures (page 198). In addition to serving as the source of other compounds of potassium, it is used chiefly as a fertilizer. Most of the potash sold for fertilizer is potassium chloride, and 90 per cent of all the potash used in this country is used as fertilizer.

Potassium bromide and potassium iodide are prepared by adding the halogen to a hot concentrated solution of potassium hydroxide. For iodine the reaction is



The solution is evaporated to dryness and is then heated with powdered carbon to reduce potassium iodate to the iodide. After filtration to remove the excess of carbon, the potassium iodide is recovered by crystallization and may be purified by recrystallization.

The iodide and bromide are used in preparing the corresponding silver salts, which are used in making the plates, films, and printing paper used in photography. They

also have some use in medicine, the bromide being used as a nerve sedative.

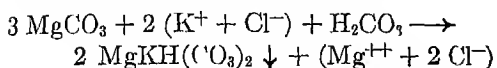
24 Potassium Hydroxide

Potassium hydroxide is prepared electrolytically in a manner similar to the electrolytic preparation of sodium hydroxide, or it is made by treating potassium carbonate, in solution, with slaked lime. In either case, the solution is evaporated, and impurities, such as the chloride, are removed by crystallization. The hydroxide is then recovered by evaporation to dryness, and the solid is melted and cast into sticks, which usually contain considerable water. Potassium hydroxide is very deliquescent, and since it absorbs water readily, it is used as a dehydrating and drying agent. It is sometimes used to remove water and carbon dioxide simultaneously from air and other gases. It removes carbon dioxide by reacting with it to form potassium carbonate. Its solution is strongly basic in character. It is more expensive than sodium hydroxide, and its use is consequently limited because the cheaper sodium hydroxide almost always serves equally as well.

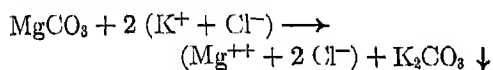
25 Potassium Carbonate (K_2CO_3)

Potassium carbonate cannot be made by the Solvay process. In preparing sodium carbonate this process can be used, because sodium bicarbonate can be precipitated from the mixture of brine, ammonia, and carbon dioxide (page 382). Potassium bicarbonate, however, is more soluble and does not precipitate. It can be prepared by heating potassium sulfate with carbon, which reduces the sulfate to potassium sulfide. The sulfide is then mixed with calcium carbonate and heated to form potassium carbonate and calcium sulfide by double decomposition. It is also made by electrolysis (page 383) and by leaching wood ashes (page 390). In the plant, or its products, potassium exists as salts of organic acids, such as tartaric ($H_2C_4H_4O_6$) or oxalic ($H_2C_2O_4$). Thus, we find cream of tartar ($KHC_4H_4O_6$) in grapes, and potassium acid

oxalate (KHC_2O_4) in rhubarb. When plants containing these substances are burned, the carbon is converted into carbon dioxide, which then gives potassium carbonate by combining with potassium oxide, which is also one of the direct products of the combustion. Potassium carbonate is also prepared by passing carbon dioxide into a solution of potassium chloride in which powdered magnesite (MgCO_3) is suspended.



The precipitate of $\text{MgKH}(\text{CO}_3)_2$ is filtered off and heated, whereupon it decomposes to form MgCO_3 , K_2CO_3 , and carbonic acid ($\text{CO}_2 + \text{H}_2\text{O}$). If the residue is mixed with water which is saturated with potassium chloride, more potassium carbonate may be obtained from MgCO_3 .



This reaction depends upon the use of an excess of potassium chloride and upon the very soluble character of magnesium chloride as compared with potassium carbonate.

Potassium bicarbonate is prepared by saturating a solution of the normal carbonate with carbon dioxide and evaporating the solution. The carbonate is used in the manufacture of several salts of potassium and in the manufacture of glass and soap.

26 Potassium Nitrate (KNO_3)

This substance, commonly called saltpeter, was widely used by the alchemists. Until about 1904, it was essential in warfare for the production of black gunpowder, but smokeless powders and other forms of explosives have now completely replaced black gunpowder, which is a mixture of potassium nitrate (saltpeter), sulfur, and charcoal. The three components must be finely ground and thoroughly mixed to promote extremely rapid combustion, since the value of the mixture as an explosive depends upon the liberation of a large volume of gases

instantaneously when ignited. The gases consist chiefly of free nitrogen, sulfur dioxide, carbon monoxide, and carbon dioxide. The potassium nitrate provides the oxygen to oxidize the carbon and sulfur and also adds its reduced nitrogen, which contributes to the increase in volume attending the reaction. Several solid substances are also produced, including the carbonate, sulfide, and sulfate of potassium. These substances, mixed with particles of unburned carbon and sulfur, are responsible for the smoke that results from the explosion.

Gunpowder was first used in military operations in the Battle of Crécy (1346). At one time, most of the potassium nitrate used to make this explosive was produced by allowing nitrogenous organic material to decompose in the presence of potassium carbonate. Until recently, potassium nitrate was prepared from Chile saltpeter (NaNO_3). To understand the process employed for this purpose, the student is referred to Figure 92. Hot saturated solutions of sodium nitrate and potassium chloride are mixed. When the solution is evaporated at a high temperature, salt first crystallizes, since it is the least soluble of the four substances that can be formed from the four ions present. As evaporation is continued, more and more sodium and chloride ions are removed by the crystallization of salt, and the concentration of the potassium and nitrate ions left in the solution becomes greater and greater. When the concentration of these ions becomes equal to 130–140 g. of potassium nitrate per 100 g. of water, the salt crystals are removed from the hot solution, which is then allowed to cool. Salt has about the same solubility in cold water as in hot, hence very little additional sodium chloride crystallizes as the solution is cooled. The solubility of potassium nitrate decreases very rapidly, however, as the temperature falls, and therefore the crystals that form when the solution is cooled consist largely of the nitrate. This may be purified by again dissolving in water and repeating the process of fractional crystallization.

Potassium nitrate is also produced by means of the reaction between nitric acid and potassium chloride, and by the reaction of potassium chloride and nitrogen dioxide, which is made by oxidizing ammonia.

Potassium nitrate forms white, rhombic crystals. It melts at 336° . It dissolves in water with the absorption of a relatively large amount of heat. Since it is not deliquescent, while sodium nitrate is, it is more desirable than the latter in the manufacture of gunpowder. It is a vigorous oxidizing agent, especially when used as the fused salt. When heated, it decomposes to form potassium nitrite and oxygen (page 67). Because it contains both potassium and nitrogen, it is a very valuable fertilizer. It is still used to manufacture black gunpowder for use in fireworks and in some blasting operations. It is also used in medicine and in curing meats. The red color of cured meats, such as "corned beef," is attributed to the use of potassium nitrate.

LITHIUM, RUBIDIUM, AND CESIUM

27. Lithium

This element was discovered in the form of its compounds, by Arfvedson, in 1817. Its name signifies "stone." Its chief sources are minerals of which *lepidolite* (California and Maine) and *amblygonite* (South Dakota) are the most important. Lithium compounds are present in small amounts in many igneous rocks. When these rocks decompose, the salts of lithium, along with those of potassium, sodium, and other metals, find their way into the soil and ground waters. Certain plants take up small amounts of lithium salts from the soil and, as in the case of potassium, the lithium appears as the carbonate in their ashes. This is true, particularly, of beets and tobacco. Many mineral waters contain lithium carbonate or other salts of this element; these are called "lithia waters."

The metal resembles potassium and sodium, both physically and chemically. It is prepared in the same manner. It is interesting as the lightest of the metals, its density is about one half that of water. The metal reacts directly with many elements, including nitrogen with which it readily

forms the nitride, and hydrogen with which it forms the hydride. The latter substance is interesting since its fused state appears to contain *negative* hydrogen ions, when the fused lithium hydride is electrolyzed, hydrogen is liberated at the anode. The metal is used in a few alloys. Some of its most important compounds are lithium chloride (LiCl), lithium bromide (LiBr), lithium carbonate (Li_2CO_3), and lithium phosphate (Li_3PO_4). The carbonate and phosphate differ from the corresponding compounds of sodium and potassium in being only slightly soluble in water. The compounds of lithium find some use in medicine, in compounding artificial mineral waters, in manufacturing glass and enamel, and in producing red light in fireworks and other pyrotechnical materials. The last-named use depends upon the red light which lithium and its volatile compounds emit when heated in a flame.

28. Rubidium

The name of this element signifies "dark red" and refers to the red lines in the spectrum of the light that rubidium and its compounds emit when they are made luminous. The element was discovered by Bunsen in 1861. Some rubidium occurs with potassium in carnallite and with lithium in lepidolite. It is also found in the ashes of some plants (beets and tobacco), and must therefore be present in small amounts in the soil. The metal may be prepared by heating its chloride with *masch metal*, which contains several of the so-called rare-earth metals. It resembles potassium and sodium but is considerably more active. Its compounds resemble those of the other elements of the family.

29. Cesium

Cesium was discovered by Bunsen in 1860. Its name means "sky blue" and refers to blue lines in the element's spectrum. Small amounts of it occur in the soil, in plant ashes, in carnallite, and in lepidolite. The most important source, however, is the

mineral *pollucite*, which is a cesium aluminum silicate found in New England. Cesium forms compounds which are similar to those of the other alkali metals. It is the most electropositive of all the elements. At temperatures above 28.5° it is a liquid. In the air it oxidizes with almost explosive violence. Cesium is used in manufacturing an alloy used in radio tubes. Both cesium and rubidium are used in making photoelectric cells. This use depends upon the property of these metals to emit electrons when they are exposed to light.

30. Identification and Separation of the Alkali Metals

The alkali metals may be detected by examining the color of the Bunsen flame which results when a platinum wire is dipped in a sample of the material under examination and then placed in the flame. This method is not satisfactory if more than one of the alkalis, or other metals which color the flame, are present. If both sodium and potassium are present, the yellow light of sodium can be absorbed by a piece of blue glass, which transmits the violet color of the potassium flame. The light from the flame may be analyzed accurately, however, by means of the spectroscope (page 231). Although two elements may emit light of almost the same color, when they or their compounds are made luminous, the spectroscope will separate these colors and will show characteristic lines corresponding to different wave-lengths. Spectroscopic methods are used, almost exclusively, to detect lithium, rubidium, and cesium.

Sodium may be detected by the two yellow lines in its spectrum. It may also be detected and separated from other ions by forming slightly soluble salts of the metal. Some of these salts are: sodium pyroantimonate ($\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$), sodium fluosilicate (Na_2SiF_6) and sodium magnesium uranyl acetate ($\text{NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 9 \text{H}_2\text{O}$).

Potassium is detected by the violet color which it imparts to the flame or by the formation of the following salts which are slightly soluble:

Potassium fluoroborate (KBF_4)

Potassium cobaltic nitrite ($\text{K}_3\text{Co}(\text{NO}_2)_4$)

Potassium perchlorate (KClO_4)

Potassium picrate ($\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK}$)

Potassium fluosilicate (K_2SiF_6)

Potassium acid tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$)

Lithium may be separated from the other alkali metals by making use of the fact that its carbonate and phosphate are much less soluble in water than the same salts of the other elements of the family.

Review Exercises

1. Enumerate the products which are formed and the chemical changes that occur at the electrodes when (1) an aqueous solution of sodium chloride is electrolyzed and (2) fused sodium chloride is electrolyzed.
2. Why is it not commercially practical to produce sodium hydroxide by the reaction of metallic sodium with water?
3. Why is sodium classified as a metal?
4. Compare the advantages of producing sodium hydroxide electrolytically with those of the process in which sodium carbonate and slaked lime are used.
5. Why is sodium hydroxide classified as a base?
6. Ten liters of normal sodium hydroxide solution are prepared by allowing metallic sodium to react with 1000 ml of water and then diluting the solution to 10 liters. How much sodium was used?
7. What weight of sodium carbonate must be used with an excess of calcium hydroxide to produce 100 lbs of sodium hydroxide? Assume that there is no loss in the process.
8. What impurities are usually present in the sodium hydroxide produced by the electrolytic process? What impurities are present in sodium hydroxide that has been exposed to the air?
9. What volume of half normal ($N/2$) sulfuric acid solution is required to neutralize 10 liters of normal sodium hydroxide solution?
10. How would you proceed to obtain a very nearly pure sample of sodium chloride from sea water?
11. What is the original source of the salt in the sea? What is the explanation of the origin of the deposits of sodium chloride that are found in various regions of the world?
12. Why does potassium chloride cost more than sodium chloride?
13. Starting with 100 lbs of salt, what weight of

sodium carbonate could be produced by the Solvay process?

- 14 Identify the following substances or materials, which have been described in this chapter: sal soda, soda ash, albite, orthoclase, lepidolite, pollucite, sylvite, cancrinite, potash, caustic soda, baking soda, Glauber's salt, rock salt, halite, gunpowder, lye, antacid.
- 15 What substances would you use and how would you proceed to prepare the following substances from the sources indicated?
 KNO_3 from KCl
 K_2S from K_2SO_4
 K_2SO_4 from KCl
 K_2CO_3 from KCl
- 16 Which of the alkali metals should francium resemble most closely? What would be some of the most likely sources of this element?
- 17 What is the common structural feature possessed by the atoms of all alkali metals? From the atomic weights and atomic numbers of the elements of this family, state (1) the number of protons and neutrons in the nucleus of an atom of each and (2) the number of electrons in each group or level.
- 18 Which of the elements of this group most readily forms positive ions? Which is least active in this respect? Account for the difference.
- 19 What are the sources of potassium compounds in the United States?
- 20 Compare the members of this family of elements with respect to the properties listed below: activity, formulas of oxides, chlorides, and sulfates, colors which they impart to a flame, density, melting point, and boiling point, physical state at ordinary temperature, solubility of salts, etc. Supplement data from text with data from handbooks and other sources.
- 21 What weights of ammonia, carbon dioxide, and salt are required to produce a ton of sodium carbonate by the Solvay process? Although an excess of some of these raw materials is used in practice, base your calculations upon the minimum quantities required.
- 22 What weight of sodium hydroxide can be produced from two tons of sodium carbonate by the reaction employing calcium hydroxide?
- 23 What weight of salt would be required to pro-

duce the sodium sulfate used in this country annually — 400,000 tons? (It is not, however, all made from salt.)

- 24 If the hydrogen chloride produced at the same time (see question 23) were dissolved in water to make a solution containing 36 per cent of HCl and having a density of 1.18, what would be the volume, in liters, of this solution?
- 25 What weight of iodine will react with the sodium thiosulfate that can be produced from 100 g of sodium sulfite?
26. A sample of pure sodium carbonate was treated with excess hydrochloric acid, and the carbon dioxide liberated occupied a volume (standard) of 224 ml. What was the approximate weight of the original sample?

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SOLUTIONS OF ELECTROLYTES

I came to my professor, Cleve, whom I admire very much, and I said, "I have a new theory of electrical conductivity as a cause of chemical reactions" He said, "This is very interesting," and then he said, "Goodbye"

ARRHENIUS

1 Introduction

At different times in our earlier discussions, we have used the term *ion*, and we have referred to solutions of different acids, bases, and salts as solutions containing ions. We have learned to think of an ion as an atom or radical that possesses an electrical charge. Substances such as sodium chloride are ionized in their crystalline state, and atoms and molecules of gases can be ionized by subjection to bombardment by electrons or alpha particles or by exposure to X-rays. In the study of chemistry, however, we are concerned primarily with the ions that exist in solutions.

In the chapter dealing with atomic structure, we have learned that the electrical charges of ions are acquired when single atoms or the atoms of radicals possess more or fewer electrons than the number they possess in their free state. A positive charge results when an atom loses electrons, a negative charge is acquired when an atom gains electrons. The number of units of charge that an ion possesses is equal to the number of electrons that the atom has gained or the number that it has lost. Since substances such as sodium chloride and sodium hydroxide are composed of ions even in the crystalline form, it is reasonable to assume that these substances exist in solutions, also, as ions. Acids, such as hydrochloric, may form ions when they react with

molecules of the solvent (page 155) in which they dissolve, and they may also form ions when they react with other substances (bases) that can accept protons from them.

This much we have already learned about ions in preceding chapters. We shall now proceed to deal more specifically and more thoroughly with the subject of ionization and of the properties of solutions that contain ions. Our ideas and theories on this subject have changed materially as more and more information has been acquired concerning the behavior of such solutions. After a brief discussion of early views of the properties and behavior of solutions containing electrolytes, we shall first study the comprehensive theory of ionization formulated by Arrhenius at a time when little or nothing was known about the structure of matter and when all substances were thought to be composed of molecules. We shall then see how this theory has been modified, in some respects, to bring it into closer harmony with our knowledge of the structure of the atom, the structures of crystals, and the general composition and behavior of electrolytes.

2. Early Views on the Behavior of Electrolytes

The terms *electrolyte* and *non-electrolyte* were first used by Faraday in his investigations of solutions as conductors of the electrical current. Faraday assumed that a solution which conducted the current contained particles moving through the liquid medium between the two electrodes.

and carrying the current across with them. It was almost necessary to think of these particles as themselves possessing electrical charges, in order to explain why some of them moved toward the negative electrode while others moved toward the positive electrode. Faraday termed these particles *ions*, a name derived from a Greek word meaning "to go." He called the ions which moved toward the positive electrode (anode) *anions* and those which moved toward the negative electrode (cathode) *cations*. The cations were thought, therefore, to carry a positive charge and the anions a negative charge. Faraday believed that these ions were produced from uncharged molecules of the electrolyte under the influence of the difference of potential between the two electrodes. In other words, it was thought that sodium chloride existed in solution as *molecules* until two electrodes, which were connected to the two terminals of a battery, were immersed in the solution, whereupon the potential between the electrodes pulled the two parts of the molecule away from each other. Many uncertainties existed in the theory. It was difficult to say whether the difference of electrical potential between the electrodes split up all the electrolyte, or if not, just what molecules, or molecules in what part of the solution, were affected. One explanation which was suggested is diagrammed in Figure 191. It was said that the molecule nearest the anode gave up a chlorine atom to be liberated at this electrode; the molecule next in line then passed its chlorine atom on to the sodium from which the chlorine atom was first separated, and so on from molecule to molecule across the solution. Similarly, at the cathode the molecule nearest this electrode allowed a sodium atom to be liberated, whereupon the molecule next in line shifted its sodium atom to the first, and so on from molecule to molecule. This explanation did not meet with

any lasting favor, however, because many facts learned about conducting solutions soon made it evident that the passage of the current and the impression of the electrical potential between the two electrodes had nothing to do with the formation of ions in the solution. It became more and more apparent that the solutions contained ions even before electrodes were placed in them. The recognition of this condition marked the next step in the development of the theory of ionization.

ARRHENIUS'S THEORY OF IONIZATION

The conclusion announced in the last sentences of the preceding paragraph was the central idea that Svante Arrhenius presented in his doctor's dissertation in 1887. His thesis concerned the behavior of solutions of electrolytes, and contained several assumptions, all of which had to do with the independent existence of ions in solutions which conduct the current. Until quite recently, these assumptions constituted our theory of ionization or *electrolytic dissociation*. For several years Arrhenius's theory served as the sole guide and working hypothesis for investigations into the properties of solutions of electrolytes and into reactions between electrolytes in solution, and even at present, it is still extremely useful and important, although some of the original assumptions have been replaced by new and in some instances, radically different concepts. These changes are to be regarded, however, as modifications of the original theory of Arrhenius rather than as parts of an entirely new theory that has been evolved to explain the behavior of electrolytes in solution.

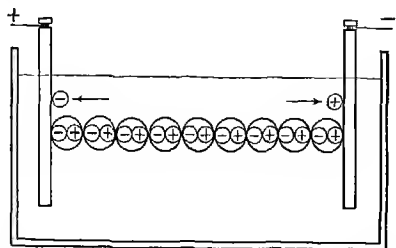


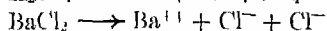
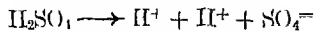
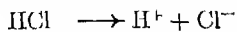
Figure 191 An Early Explanation of the Action of Electrolytes

3 A Brief Summary of Arrhenius's Theory

Before attempting to present the many lines of evidence that support it, we shall summarize, very briefly, the essential points in Arrhenius's original theory.

(1) Ions are produced by the *dissociation* of *molecules* of salts, acids, and bases in certain solvents, of which water is the most important.

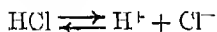
(2) Ions are electrically charged. When a molecule dissociates, it produces one or more positively charged ions and one or more negatively charged ions. The sum of the charges on all the positive ions produced by a molecule is equal to the sum of the charges on all the negative ions produced by the same molecule.



The solution, therefore, remains electrically neutral.

(3) Those compounds whose aqueous solutions do not conduct the electrical current do not produce any ions.

(4) The ionization of an electrolyte is not complete except in extremely dilute solutions. In ordinary solutions the ions produced by the dissociation of molecules are in equilibrium with undissociated molecules.



Each electrolyte is assumed to have a specific ionizing tendency, hence, the percentages of the molecules of different electrolytes which must ionize to establish equilibrium differ widely. The ability of the solution of an electrolyte to conduct the current is assumed to depend upon the degree of ionization of the solute. When the solution is made more dilute, it is assumed that a greater quantity of the electrolyte exists in the ionic rather than the molecular state, that is, the percentage of ionized electrolyte increases. In the more dilute solutions, the ions are more widely scattered, and the chances that they will meet and recombine are fewer.

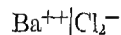
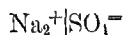
4 Evidence that Supported the Theory

Let us now examine some of the facts upon which the theory of Arrhenius was based. In studying these facts, *let us understand that we are interpreting them as Arrhenius did*. Later, we shall examine the same facts again and, in some instances, we shall learn that somewhat different interpretations are not only possible but are now preferred. For the present, however, we shall examine certain properties of the solutions of electrolytes just as Arrhenius studied them in 1887, and we shall see how he ex-

plained them and why he explained them as he did.

5. Reactions Between Electrolytes in Solution

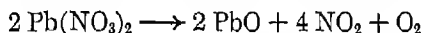
One of the first indications that salts, acids, and bases form ions in aqueous solutions was observed when the reactions of these substances in solution were compared with the reactions of the same substances in the solid, or dry, condition. The effect of water in promoting the chemical activity of many substances has already been mentioned in several instances (e.g., page 348). Sometimes, as in some reactions involving oxidation, water appears to act as a catalyst. In other reactions involving (usually) double decomposition between salts, acids, and bases, water appears to make the double decomposition possible. Reactions of this kind, which do not occur when the dry substances are mixed, occur easily and rapidly when the substances are first dissolved in water and the solutions are mixed. In double decomposition, the reacting substances, *if they consist of molecules*, must first dissociate into *parts* of molecules, and these parts then recombine in a different way to produce new substances. Thus, in the reaction of sodium sulfate and barium chloride, each substance appears to dissociate first into two parts.



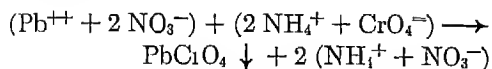
Barium then combines with the sulfate radical to produce barium sulfate, which precipitates from the solution, since it is very slightly soluble. If this substance is removed by filtration, and the filtrate is evaporated to dryness, crystals of sodium chloride are formed. The formation of the precipitate of barium sulfate is almost instantaneous, a fact which indicates that the barium and the sulfate particles exist in solution independently of the other parts of their original compounds, and that they do not have to be liberated as the reaction proceeds. If finely powdered barium chloride and sodium sulfate are mixed, no noticeable reaction occurs.

The failure of a reaction to occur under these conditions indicates that conditions for a double decomposition are not favorable, Arrhenius interpreted this failure as an indication that barium and sulfate ions were produced only in solutions of the salts, and that these particles therefore could not combine to form barium sulfate until the original substances were dissolved.

A more definite and convincing example of a similar character may be observed by mixing lead nitrate and ammonium chromate first in the dry, powdered state and then in solution. For the dry substances, there is no indication of a reaction of any kind at ordinary temperature. When the mixture is heated, a reaction does occur, changes in the color of the mass become apparent, and gases, which also may be colored, are evolved. But each substance acts in the same manner, when the mixture is heated, as it would if it were heated alone, in short, each decomposes more or less in its own way. Lead nitrate, for example, decomposes to form the oxide, free oxygen, and nitrogen dioxide (brown)

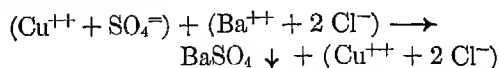


When solutions of lead nitrate and ammonium chromate are mixed, a very definite reaction occurs immediately, and a yellow precipitate of lead chromate forms. If lead chromate is removed by filtration, and the filtrate is evaporated, ammonium nitrate is obtained as the other product of the reaction



Here again, double decomposition, which occurs very easily in solution, fails to occur in the dry state of the reactants. The most plausible reason for the failure is that the parts of the original substances from which the products are formed are not free and intimately mixed in the solid state. In solution, the different particles appear to be ready to combine as soon as the two substances are mixed.

The particles of salts, acids, and bases that participate in double decomposition reactions are the same particles of these substances that migrate toward the electrodes when solutions of these substances are electrolyzed. Thus, cupric sulfate always reacts in aqueous solutions, whenever it takes part in a double decomposition, to form a new copper compound and the sulfate of some other element



The same particles (Cu^{++} and SO_4^{--}) of cupric sulfate migrate toward the electrodes during the electrolysis of a solution of this salt. In neither case do such particles as CuS and O_2 or CuSO and O_2 ever appear. Furthermore, the barium from any soluble barium salt or from barium hydroxide, $\text{Ba}(\text{OH})_2$, and the sulfate radical from any soluble sulfate react always in solution to form the same product (BaSO_4).

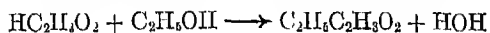
6 Reactions of Electrolytes and of Non-Electrolytes Compared

Compounds whose solutions do not conduct the electrical current do not enter into double decomposition reactions at all readily, and many of them do not take part at all in this kind of chemical change. The reactions in which they do participate are not as definite as the reactions that occur in solutions of acids, bases, and salts, nor can the results of such reactions be predicted as simply or as accurately as can be done for the reactions of salts, acids, and bases. Furthermore, reactions between non-electrolytes are much slower, as a rule, than reactions between electrolytes.

Basing our arguments upon such facts as were known to Arrhenius, it would be possible, of course, to assume that reactions between electrolytes in solutions involve whole molecules of the reactants, but our assumption would not be at all probable. If it were, a reaction could not occur until the necessary number of molecules of each

kind met. The molecules would then have to dissociate into parts before the new substances could be formed, and the course of the reaction would therefore involve several steps, the final product could be formed only after the first steps had occurred. It is difficult to believe that reactions could be as nearly instantaneous as most of the reactions of electrolytes are, if they followed such a step-by-step course.

It is interesting in this connection to compare the reaction of two electrolytes, such as hydrochloric acid and sodium hydroxide, with the reaction between acetic acid and ethyl alcohol



The former is practically instantaneous. The second reaction proceeds very slowly, at ordinary temperature, it is going on even after several weeks. Both reactions are double decompositions. The difference in speed must result from differences in the number of particles that are free at any one time to form the products of the reaction. Ethyl alcohol is classed as a non-electrolyte, and hence we should not expect to find, either in the pure state or in solution, that it contains ethyl and hydroxyl particles. The fact that the reaction in which these radicals combine with the H^+ and $\text{C}_2\text{H}_3\text{O}_2^-$ particles of acetic acid is extremely slow is a fair indication that ethyl alcohol does not dissociate into such particles in solution.

Another interesting example of the difference between electrolytes and non-electrolytes is shown in the behavior of sodium chloride as compared with carbon tetrachloride (CCl_4) or chloroform (CHCl_3). Any soluble chloride, such as NaCl , reacts immediately in solution with silver nitrate to form silver chloride, which precipitates as a white, "curdy" substance, but when silver nitrate is added to carbon tetrachloride or chloroform no such reaction occurs. This can only mean that in substances such as sodium chloride, the chlorine is relatively free to combine with silver, and that the silver of silver nitrate is free to combine with chlorine, but in carbon tetrachloride

and chloroform the chlorine is not free, and silver chloride cannot be formed.

All of the differences that we have noted between the behavior of electrolytes and non-electrolytes indicate that the former produce ions in their solutions and that the latter do not. It must be admitted, however, that the evidence from this source is not entirely conclusive. The suggestion that ions must be present in certain solutions and absent in others encourages a search for more conclusive evidence in other directions. Such evidence is not difficult to find.

7 Abnormalities of Solutions of Electrolytes

One of the most important lines of evidence that led Arrhenius to conclude that solutions of salts, acids, and bases contain ions deals with the vapor pressures, boiling points, freezing points, and osmotic pressures of these solutions. From our study of solutions we have found that very definite regularities may be expected of solutions with respect to these four physical properties. To be exact, we have learned that *all solutions which contain one gram-molecular weight of any solute in 1000 g of a given solvent should have, if the solute is composed of molecules and if these molecules remain chemically unchanged when the solution is made, the same vapor pressure, boiling point, freezing point, and osmotic pressure*. We have interpreted these regularities as meaning that the effect of the solute in each of these four respects is proportional to its mole fraction in the mixture, the effect of the solute in lowering the freezing point of the solvent, for example, depends only upon the number of molecules (or particles) of the solute mixed with a certain number of molecules (the number in 1000 g) of the solvent. The molecules of one substance produce the same effects as the molecules of another substance.

When we observe the vapor pressures, boiling points, freezing points, and osmotic pressures of solutions of electrolytes, we find, however, that these regularities no longer

exist. We call these departures from the normal or regular behavior of solutions the *abnormalities* displayed by solutions of electrolytes, and upon them rests one of the most decisive arguments in favor of the ionization theory. Let us consider specific cases.

8. The Abnormal Boiling Points of Solutions of Electrolytes

We might expect that a solution containing one gram-molecular (or gram-formula) weight of sodium chloride in 1000 g of water would boil at the same temperature as a sugar solution of the same concentration, i.e., it should boil at 100.52°. This would be true if, as Arrhenius thought, sodium chloride were composed of molecules, and if these molecules were not changed into ions when they dissolved in water. The solution of sodium chloride boils, however, at 100.97°, and the elevation (0.97°) of the boiling point is almost twice the elevation produced by a gram-molecular weight of sugar dissolved in the same weight of water. How can this be? Arrhenius answered this question — still assuming that undissolved sodium chloride is composed of molecules — as follows:

(1) The elevation of the boiling point depends solely upon the relative number of particles of solute mixed with a definite number of molecules of the solvent. This general principle appears almost certainly true as we study the effect of non-electrolytes upon the boiling point of the solvent.

(2) Gram-molecular weights of all substances contain the same number of molecules. Hence, if we dissolve gram-molecular weights of sugar and salt in the same weights of water, we should form solutions containing the same number of molecules. These solutions should boil, therefore, at the same temperature. But they do not.

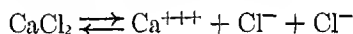
(3) The boiling point of the salt solution indicates, in accordance with (1), that this solution contains almost twice as many solute particles as the sugar solution.

(4) The conclusion reached in (3) can be true only if almost all of the molecules of salt — if salt is composed of molecules — break up in the solution, each molecule forming two particles,

and if each particle has the same effect as a whole molecule of sugar. The fact that the elevation of the boiling point is not quite twice as great as the elevation caused by an equal number of sugar molecules indicates that not all of the molecules of salt break up in the solution. The solution may therefore contain some molecules that are not ionized.



The elevation of the boiling point for a solution containing one gram-molecular weight of calcium chloride (CaCl_2) in 1000 g of water is between two and three times as great as the elevation produced by one gram-molecular weight of sugar. This abnormal effect can be explained if we assume that almost all of the molecules of calcium chloride break up into three ions each.



Similarly, the elevation of the boiling point for a solution containing one gram-molecular weight of ferric chloride (FeCl_3) in 1000 g of water approaches four times the normal elevation. In other cases, the elevation is only a very little more than the normal elevation of 0.52°, but it is definitely greater than this value. Only a very few of the molecules of the solute in these solutions appear, therefore, to ionize.

9. The Abnormal Freezing Points of Solutions of Electrolytes

The lowering of the freezing point of water by non-electrolytes is as regular as the elevation of the boiling point. Molal aqueous solutions of sucrose, glucose, and glycerine freeze at -1.86° . But for solutions of electrolytes abnormal lowering of the freezing point is observed, and the extent to which the effect is abnormal is of the same order of magnitude as the abnormal elevation of the boiling point by the same solute. Thus, the freezing point of a solution containing one gram-molecular weight of sodium chloride in 1000 g of water is -3.42° , which is almost twice the normal lowering of the freezing

point in a molal solution. It is actually $\frac{3.42}{1.86} = 1.84$ times as great. Here again, we must assume that almost all of the molecules in the gram-molecular weight of salt — if it consists of molecules — break up to form two particles (ions) each. The ratio of the lowering of the freezing point for the sodium chloride and for the same concentration of a non-electrolyte is approximately the same as the ratio of the elevations of the boiling point in the two solutions. The latter ratio is $\frac{0.97}{0.52} = 1.84$. The fact that the two ratios are approximately equal indicates that the same number of particles are present in the sodium chloride solution at the boiling and freezing points of the solution.

10 The Osmotic Pressure of Solutions of Electrolytes

We have learned (page 212) that the osmotic pressure of dilute solutions of non-electrolytes is directly proportional to the number of molecules of solute present in a solution containing a fixed number of molecules of solvent. We have seen, also, that solutions containing the same number of molecules of different non-electrolytes (per 1000 g. of solvent) have the same osmotic pressure. These solutions must therefore contain the same number of particles of the different solutes. If we compare the osmotic pressures of solutions of non-electrolytes with those of solutions containing the same molal concentrations of acids, bases, and salts the latter are found always to be greater than the former. Once again we must conclude that the solutions of electrolytes contain a greater number of particles than corresponds to the molecular concentration, and that at least some of the solute molecules ionize in the solution. Since the osmotic pressure depends upon the relative number of *particles* of solute, each ion has the same effect upon the osmotic pressure as an entire molecule would have.

11. The Molecular Weights of Electrolytes

The molecular weights of non-electrolytes can be determined from the boiling points and freezing points of their solutions in suitable solvents. This method was described and illustrated in the chapter that deals with solutions (page 212). When the same method is applied to salts, acids, and bases, the molecular weights calculated from freezing- or boiling-point data are always too small. We should expect such results, since the method of determining the molecular weights upon the principle that a definite number of particles (6.02×10^{23}) will produce a definite elevation of the boiling point (0.52° for water) and an equally definite lowering of the freezing point (1.86°) when dissolved in 1000 g. of solvent. Now the ions which are produced in solutions of electrolytes have the same effect upon the properties of the solution as whole molecules. The freezing point of a solution containing in all 6.02×10^{23} sodium and chloride ions in 1000 g. of water would be -1.86° . Similarly, a solution containing the same weight of water and a total of 6.02×10^{23} sodium ions, chloride ions, and sodium chloride molecules would freeze at the same temperature. It is evident, therefore, that we cannot take the weight of sodium chloride, or the weight of any other electrolyte, which lowers the freezing point of 1000 g. of water to -1.86° , as the gram-molecular weight, if by the gram-molecular weight we mean the weight of the substance that contains 6.02×10^{23} molecules of the substance.

A solution containing 58.46 g. (the gram-molecular weight) of sodium chloride in 1000 g. of water freezes at -3.42° . Using the ordinary procedure for calculating molecular weights, we should set up the following proportion and solve for x , the molecular weight of sodium chloride:

$$\begin{array}{ccccccc} 3.42^\circ & 1.86^\circ & 58.46 & x \\ & & x & = 31.8 \end{array}$$

From this evidence alone, we should conclude that the molecular weight of sodium chloride is 31.8. This number corresponds, however, to an impossible formula — approximately $\text{Na}_{1/2}\text{Cl}_{1/2}$ — and cannot be correct, the simplest possible formula is NaCl , which corresponds to a molecular weight of 58.46. The difficulty arises, evidently, because the 6.02×10^{23} particles that lower the freezing point to -1.86° consist of approximately

3.02×10^{23} sodium ions and 3.01×10^{23} chloride ions and not 6.02×10^{23} molecules of sodium chloride

12 Percentage of Ionization

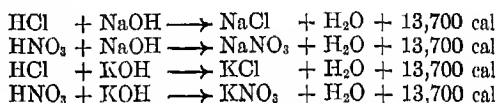
From the data presented above, it is possible to calculate — *upon the basis of Arrhenius's theory* — the percentage of sodium chloride molecules in the molal solution that ionize and the percentage of those that do not. If the solution froze at -1.86° , it would be evident that the number of particles (in 1000 g of water) corresponds exactly to the number of molecules in a gram-molecular weight of the solute, hence we should decide that none of the molecules in this solution is ionized. To take the other extreme, if the freezing point of the solution were -3.72° it would appear that each molecule produces two ions, and that 100 per cent of the molecules are ionized. Actually, the freezing point is -3.42° , which is between -1.86° and -3.72° . Hence a number of molecules, somewhere between zero and 100 per cent of the entire number present, appear to be ionized. The apparent percentage of ionized sodium chloride can be calculated easily from these facts. If the solute were completely ionized, the lowering of the freezing point *in excess of the normal value* would have been $3.72^\circ - 1.86^\circ = 1.86^\circ$. Instead, the freezing point is lowered $3.42^\circ - 1.86^\circ = 1.56^\circ$ more than it would be if no sodium chloride were ionized. The percentage of ionized solute is, therefore, $\frac{1.56}{1.86} \times 100 = 84$ per cent.

For some solutes the freezing points of molal solutions are only slightly lower than -1.86° . The percentages of ionization of these substances are very small, such substances are classified as weak electrolytes. From freezing-point data, it may be shown that the apparent degree of dissociation of acetic acid (molal concentration), for example, is only about 13 per cent. The apparent degrees of ionization of other salts, acids, and bases are given in Table 23 on page 437.

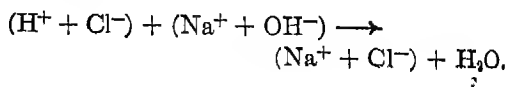
13 Heats of Neutralization

When equal volumes of solutions containing equivalent weights of different strong acids and different strong bases are mixed, and the acids and bases neutralize each other, experimental results show that practically the same quantity of heat is liberated in each reaction.

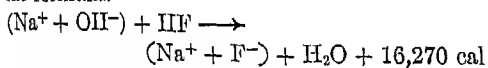
The following reactions are for normal (1 N) solutions of very strong, or active, acids and bases. (The equations are written as Arrhenius would have written them instead of in the ionic form that we use elsewhere.)



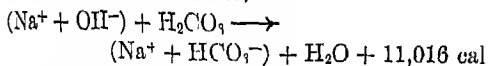
The liberation of the same quantity of heat by each of these chemical reactions indicates that one change, and only one change, occurs in each case. As the only reaction common to all is the one between hydrogen and hydroxyl groups to form molecules of water, we must conclude that the constant heat of neutralization is the heat liberated when 18.016 g of water is produced from the ions. If true, this statement means that both the base and the acid, as well as the salt, exist in the solution as independent ions. If the molecules of base and acid first had to be separated into ions, and if these ions then combined to form the salt as well as water, we could not expect that the different reactions would show the same ultimate heat change. In each reaction the only change that occurs is the formation of a molecule of water from hydrogen and hydroxyl ions. For each gram-molecular weight of water thus produced, 13,700 calories are liberated. We shall write the equation, therefore, to show that the acid and the base exist in the ionic state in the beginning, and that at the end we have ions of the salt and molecules of water.



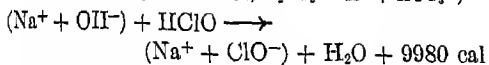
Here is one argument, therefore, to justify the ionic form of equations that we have used previously and shall continue to use for reactions of strong electrolytes. If there is logic in this argument, we should expect to find that weak acids and weak bases liberate variable quantities of heat upon neutralization. In these cases we should expect that some energy would have to be expended to separate the ions before the neutralization reaction could occur. Like other reactions, some of these changes might be exothermic and some endothermic. Hence, the ultimate heat effect may be greater than the constant heat of neutralization of strong acids and strong bases, or it may be less. The heats of neutralization of a few weak acids and bases are shown below. These values are for equivalent weights and assume fairly dilute solutions. In the equations below, strong electrolytes like sodium hydroxide are shown by ionic formulas, but weak electrolytes like hydrofluoric acid are shown by molecular formulas.



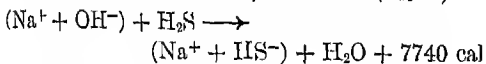
(Heat is liberated as HIF ionizes)



(Heat is absorbed by the reaction, $\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-$)



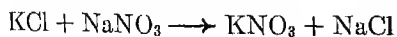
(Heat is absorbed by the reaction, $\text{HClO} \rightarrow \text{H}^+ + \text{ClO}^-$)



(Heat is absorbed by the reaction, $\text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}^-$)

14. Thermoneutrality

Let us consider a solution in which both potassium chloride and sodium nitrate are present. If this solution is evaporated at a relatively high temperature to drive off a portion of the water, and then cooled to 10° , crystals consisting chiefly of potassium nitrate will form. We might conclude, therefore, that the following reaction occurs:



If the two salts in the beginning and those at the end of the reaction exist in the molecular state, we should expect some heat change to be evident as the reaction takes place. We might expect energy to be required to

separate potassium chloride and sodium nitrate into their ions and perhaps a release of energy when these same ions combined again to form the two products. The ultimate effect might be, of course, either a positive or a negative heat of reaction. But strangely enough, solutions of these two substances (KCl and NaNO_3) may be mixed without any observable heat change at all. This result can have only one explanation: no reaction occurs in the dilute solution of these substances. We must think of the separate solutions of KCl and NaNO_3 as containing K^+ and Cl^- ions and Na^+ and NO_3^- ions, respectively. When the solutions are mixed, all four ions remain in their independent states, and here is no combination to form molecules of KNO_3 and NaCl . It is only when the solution is concentrated, by evaporation, that observable products of the reaction are obtained in the form of crystals of one or more substances.

15. Electrolysis

Thus far, the evidence which has been discussed in favor of the theory of ionization does not indicate that the particles produced in solutions of electrolytes are electrically charged. The evidence that ions are charged, and also information concerning the magnitude of their charges, is obtained by studying the electrolysis and electrical conductivity of the solutions that contain them.

Let us consider the electrolysis of a solution of hydrochloric acid. Let us assume that this solution does contain positively charged hydrogen ions and negatively charged chloride ions. Molecules of hydrogen chloride may or may not be present, we are not especially concerned with that question at this time, because such molecules, being without charge, would play no part directly in electrolysis. The two electrodes are connected to the two terminals of a storage battery, or to some other source of direct current, which maintains a difference of potential between them. In an ordinary, three-cell storage battery this difference of potential is about

six volts. As soon as the electrodes are placed in the solution, hydrogen migrates toward the cathode, and chlorine toward the anode. At the electrodes, the two elements are changed from the condition in which they exist in a solution of hydrochloric acid to the free state, and they then escape as gases from the solution.

We note, first, that the hydrogen and chlorine must be in a different state in solution as compared with their condition after they are liberated at the electrodes, there is no indication, for example, that the solution contains free chlorine. Secondly, there is clear evidence that some change occurs at the electrodes, a change that converts them from one state into the other. In the third place, we note that in the solution the two elements must be more or less independent of each other because one moves toward one electrode and the other moves toward the other electrode. Why should hydrogen move toward the electrode upon which the battery maintains a negative charge, unless its atoms in the solution are positively charged? Similarly, must not the chlorine atoms possess negative charges, since they migrate always toward the positive electrode? In what other respect could hydrogen and chlorine atoms in solutions differ from the free atoms of these elements? If the two kinds of atoms are oppositely charged in the solution, they must be uncombined. If they existed in the form of molecules of HCl , the charge of one would neutralize the charge of the other, and the electrically neutral particles would not be attracted by the electrodes. For an explanation of electrolysis based upon present-day information regarding electrolytes, refer to page 110.

16 Are Ions Produced only when an Electrical Potential is Impressed Between the Electrodes?

Our explanation of electrolysis and the electrical conductivity of solutions in the preceding section appears to be the only reasonable interpretation of these phenom-

ena, and the fact that it fits the case so well indicates convincingly that ions must exist in conducting solutions. One question, however, remains unanswered. When are these ions produced? Is it possible that they are produced when molecules are pulled apart under the influence of the potential difference that the battery maintains between the two electrodes? This question is answered in the negative, and the reasons for this answer are based upon the following considerations.

17. Faraday's Laws of Electrolysis

One of the most important contributions made by Michael Faraday to physical science has to do with electrolysis. The laws that he formulated on this subject can be summarized by the following general statement: *The quantity of any ion liberated during the electrolysis of any electrolyte depends upon the quantity of electricity that passes through the solution, the same quantity of electricity liberates equivalent quantities of different ions.*

The quantity of electricity consumed in an operation is measured in terms of *coulombs*. A quantity of electricity amounting to one coulomb, flowing through a conductor for one second, is called a current of one *ampere*. Electrical energy depends upon two factors. One of these represents the quantity of electricity and is measured in coulombs. The other is an intensity factor, which is measured in terms of *volts*. The volt is the unit of potential difference (electromotive force) which exists, for example, between the two electrodes of an electrolytic cell. We shall speak of voltage in connection with electrolysis in a later section. Faraday's law is concerned only with coulombs, or the quantity of electricity. The two factors that determine electrical energy may be compared roughly with the two factors that determine the energy possessed by water in flowing from a higher to a lower level. Here the quantity factor is measured by the amount of water transferred from one position to another. The intensity factor depends upon the difference between the two levels. If the levels are the same, the intensity factor is zero.

To liberate 1.008 g of hydrogen from a solution of any acid, 96,500 coulombs of

electricity must be used. The same quantity of electricity will liberate one gram-atomic weight of any *univalent* element. Now gram-atomic weights of all elements contain the same number of atoms. Hence we may conclude that the same quantity ($96,500/6.02 \times 10^{23}$ coulombs) of electricity is required to convert one atom of any univalent element from the ionic form into the free state. For *divalent* elements, 96,500 coulombs liberate one half of an atomic weight, for *trivalent* elements, one third of an atomic weight, and so on. Thus, the passage of 96,500 coulombs through different cells containing silver sulfate, cupric sulfate, antimony chloride, and ferric chloride, hydrochloric acid, and sulfuric acid will liberate at the cathodes of these cells 107.88 g. of silver, 31.78 g. of copper, 40.59 g. of antimony, 18.61 g. of iron, and in each of the last two cells, 1.008 g. of hydrogen. At the same time that these weights of the metals or hydrogen are liberated at the cathode, the other parts of these compounds are discharged at the anodes or, if these substances themselves are not liberated, oxygen is set free (in aqueous solution).

18. An Explanation of Faraday's Law

Since twice as much electricity (twice as many coulombs) is required to discharge one gram-atomic weight of a divalent element as is required to discharge a gram-atomic weight of hydrogen, or any univalent element, there must be twice as much electricity on each ion of the former as there is on an ion of the latter. This condition is represented in the formulas of the different ions. Thus, we write the formulas of ferrous and cupric ions as Fe^{++} and Cu^{++} , respectively, ferric and antimony ions (from SbCl_3) as Fe^{+++} and Sb^{+++} ; hydrogen and silver ions as H^+ and Ag^+ .

When we recall that the atoms of all univalent (positive) elements lose a single electron each, it is not surprising that the same quantity of electricity is required to liberate an equal number of atoms of any of these ele-

ments. The atoms of a divalent element lose two electrons each. It is therefore easy to understand why the same quantity of electricity will liberate only one half as many atoms of a divalent element as of a univalent element. Judging from the quantities of electricity required to discharge atomic weights of hydrogen and cupric ions, for example, it appears that the quantity of electrical charge on each cupric ion is twice the quantity on each hydrogen ion. This conclusion agrees completely with our ideas of the charges that these ions carry and the manner in which these charges are acquired by the atoms.

19. Decomposition Voltage

We have seen that the same *quantity* of electricity will discharge an equal number of all univalent ions, one half as many divalent ions, etc. This is true regardless of the length of time that the current passes through the solution and regardless of other conditions such as temperature and concentration. This fact, on first thought, might lead us to the conclusion that ions are present in the solution from the beginning and are not produced when the electrodes are placed in the solution. We believe this actually to be the case, but Faraday's law does not prove it to be so. If molecules had to be pulled apart to produce ions, we should expect that different quantities of *electrical energy* would be required to liberate the ions from different molecules. As already pointed out (page 408), the quantity of electrical energy consumed depends upon the voltage (or electromotive force) between the electrode as well as upon the number of coulombs of electricity used. Hence, until we have also investigated the voltages required to liberate different ions, we cannot be sure that ions are not produced by the use of electrical energy to dissociate molecules. It is true that a certain minimum electromotive force is required to liberate the ions of a given electrolyte at the electrodes of an electrolytic cell. The minimum electromo-

tive force required for a given electrolyte is called the decomposition voltage for that substance and is different for different electrolytes. Nevertheless, it is still possible to consider the ions as existing independently at all times in the solution. That different voltages are required to liberate ions carrying the same number of units of charge does not mean, necessarily, that different amounts of electrical energy are required to separate the ions from those of the opposite charge in the solution. Let us see whether or not a more reasonable explanation of minimum decomposition voltages can be offered.

20 Polarization

Let us consider a cell containing a solution of hydrochloric acid. If the electrodes are made of platinum, the hydrogen and chlorine that are liberated collect upon the electrodes after a short time. These elements have certain tendencies to change back to ions, and if they do so, these changes produce effects which are exactly opposite to the effects produced when the ions are discharged. Indeed, if the battery is disconnected from the cell, the latter acts for a short time as a battery itself. The hydrogen that has collected at the cathode ionizes and passes back into the solution as positive ions, leaving the electrode with a negative charge. At the other electrode chlorine passes into the solution as negative ions and leaves that electrode with a positive charge. Hydrochloric acid is thus reproduced and the effect of these reactions upon the voltage between the electrodes is clearly the opposite of that which must be in operation to discharge hydrogen ions at the cathode and chloride ions at the anode. The effect of the liberated elements in producing an electromotive force, and therefore a current which opposes that supplied by the battery, is spoken of as a reverse electromotive force. When this happens the cell is said to be *polarized*.

21. An Explanation of Decomposition Voltage

If hydrogen and chlorine are to be liberated continuously, it is evident that the electromotive force maintained between the electrodes by the battery must be sufficiently great to overcome the reverse electromotive force produced by the elements. In other words, the tendency of the elements to re-ionize must be overcome by supplying a voltage which is sufficiently great to discharge the ions in spite of this tendency.

In the same connection let us consider, also, the electrolysis of solutions containing equivalent weights of zinc chloride (ZnCl_2) and cupric chloride (CuCl_2). We find that a higher voltage is required to deposit metallic zinc at a platinum electrode from the solution containing zinc ions than is needed to change cupric ions into metallic copper. This is because atoms of metallic zinc have a greater tendency than copper to lose electrons, and thus to dissolve again as ions. When a solution of zinc chloride is electrolyzed, zinc is deposited on the cathode, chlorine is liberated at the anode and tends to collect on that electrode. The zinc and chlorine which are thus liberated have a certain tendency to pass back into the solution as ions. This tendency is opposed by the electromotive force which is responsible for the electrolysis of zinc chloride. If electrolysis is to proceed continuously, this reverse tendency must be overcome by an electromotive force which is supplied by the battery and which acts in the opposite direction — that is, in the direction which results in electrolysis. For the solution of cupric chloride, this required voltage is smaller than for zinc chloride, because copper has less tendency to pass back into solution as cupric ions.

In like manner other differences in decomposition voltages can be explained upon the basis of differences in the ionizing tendencies of different elements. Upon final analysis, these differences depend upon the relative ease with which the atoms of different elements give up electrons and become positive ions, or in the case of the non-metals, gain electrons and become negative ions. Hence, we find a plausible and natural explanation of decomposition voltages, which

does not in any way make necessary the conclusion that electrical energy is required to pull apart the molecules of an electrolyte, thus producing the ions that are discharged at the electrodes

If a solution of cupric chloride is electrolyzed in a cell in which the electrodes are made of copper, we find that no minimum electromotive force need be supplied by the battery. Even a very feeble current operated at very low voltage will allow electrolysis to proceed continuously. As in cells in which platinum electrodes are used, cupric ions migrate toward the cathode and are discharged, metallic copper being deposited. The chloride ions migrate toward the anode, and instead of being discharged, react with copper to reform cupric chloride. The ultimate effect, therefore, is to dissolve copper at the anode and deposit it at the cathode. The composition of the electrolytic solution remains unchanged. There are no reverse electromotive effects in this cell, hence, the only work which must be done by electricity is to cause the two kinds of ions to migrate toward the electrodes. The same condition is found in other cells of a similar nature, i.e., cells in which the electrodes react and the composition of the solution remains unchanged. Electrical energy is required only in very small quantities in any of these cases and is used only to overcome the resistance which the ions encounter in their migration. If the ions had to be torn loose from the molecules in which they exist, a minimum voltage would be required in such cells as in the others which we have mentioned. This decides the question at issue beyond serious doubt. Ions must exist in electrolytic solutions at all times and are not produced by impressing a required voltage between electrodes in the solution.

22 Electrical Conductivity

Since solutions of salts, acids, and bases act as conductors of the electric current, we may speak of their *conductivity* in the same sense as we speak of the conductivity of a copper wire. To measure the conductivity of a solution, we determine its electrical resistance by comparing the resistance of the solution with that of a metallic conductor for which the resistance is accurately known.

The unit of resistance is the *ohm* and the unit of conductivity is the *reciprocal ohm*,

$$\left(\frac{1}{\text{number of ohms}} \right)$$

The quantity of current carried by the solution in a given period of time is determined by the number of ions that reach the electrodes. Every kind of ion acts more or less independently and, under constant conditions, moves with a definite velocity, regardless of the substance from which it was produced. However, as we might expect, the migration velocity does vary with changes in the voltage and with the concentration of the solution.

Differences in the migration velocities of different ions can be shown by means of the experiment pictured in Figure 192. This figure is

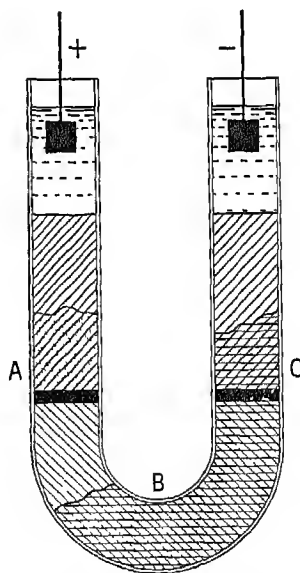


Figure 192 An Experiment to Demonstrate Differences in the Migration Velocities of Ions

The U tube is filled with gelatine or agar. The lower half of the jelly contains cupric sulfate in each arm of the tube. In the upper half of the left arm (A) there is present a small amount of barium chloride. When a current flows through the solution, the cupric ions, which are colored blue, migrate toward the cathode, thus extending the region of blue color in this direction. The rate at which this change occurs is a measure of the migration velocity of the cupric ion. The sulfate ions migrate toward the anode and at A react with barium ions to form insoluble barium sulfate. The formation of this precipitate allows us to follow the migration of the sulfate ion in this arm of the tube.

self-explanatory. The velocities of different ions may be compared by noting the relative distances they travel from their source in the same period of time. The distance a given ion travels is denoted by the relative quantity of the medium in which it produces a change in color.

We should not think of the ions in a solution as moving as rapidly as molecules of a gas. Their migration velocities are really very slow. Hydrogen ion, which has the highest velocity, migrates (at 18°) 11.74 cms. per hour in a very dilute solution under the influence of one volt. Under the same conditions, hydroxyl ion migrates with a velocity of 6.5 cms. per hour, and sodium ion with a velocity of only 1.6 cms. per hour.

Since each kind of ion always carries the same charge and moves with the same velocity (under constant conditions) it may be said to have a definite and independent conductance. The total conductance of an electrolyte, such as hydrochloric acid, is equal to the sum of the conductances of its ions (H^+ and Cl^-). The conductance of a solution depends, therefore, upon the number of ions in the solution, the charge on the ions, and their velocities.

23. The Conductances of Different Solutions

The aqueous solutions of all salts, acids, and bases conduct the current, but there is a great difference in the conductances of solutions containing equimolecular concentrations of different substances. Some of these solutions are excellent conductors and some conduct scarcely at all. The conductance of a given electrolyte varies, also, with the solvent in which it is dissolved. A substance that conducts well in aqueous solutions, conducts rather feebly in alcoholic solutions, and scarcely at all when dissolved in benzene, carbon tetrachloride, or chloroform. We must conclude, therefore, that poorly conducting solutions contain very few ions, remembering, however, that the small conductivity may be due in part to the slow velocity of the ions. The velocity may be further reduced by the resistance encountered by the ions in moving through the solvent, which contains ions carrying the opposite kind of

charge and large numbers of uncharged molecules. Attraction must exist in the solution, not only between ions of unlike charge, but also between ions and the molecules of the solvent (page 413). This attraction is of the same general character as that which exists between molecules of gases, molecules of liquids, the particles of crystalline substances, and molecules of solute and solvent. But all of these forces that restrict the movement of ions cannot explain the almost total failure of some aqueous solutions to conduct the current, a condition which can be caused only by an almost total absence of ions.

24. Specific and Equivalent Conductances of Solutions

Let us assume, as Arrhenius did, that a solution of any salt, acid, or base contains both ions and undissociated molecules. These are in equilibrium with each other (page 399). Let us start with a solution containing one equivalent weight of solute per liter. The conductance of 1 ml. of this solution, when measured between platinum electrodes which are 1 cm. square, 1 cm. apart, and under a potential of one volt, is called the *specific conductance* of the solution. The *equivalent conductance* for any electrolyte is defined as the conductance, between electrodes 1 cm. apart, of a volume of the solution large enough to contain 1 gram-equivalent weight of the solute. In

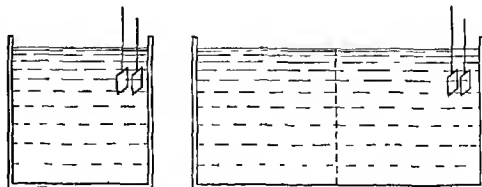


Figure 193 The Measurement of Specific and Equivalent Conductances

The volume of the solution between the electrodes is the same in both cases. If no more ions were produced upon dilution, the specific conductance in the second solution (right) would be one half of the specific conductance of the first. But there are twice as many cubic centimeters in the second solution, and hence, the equivalent conductance should not change upon dilution.

practice, the equivalent conductance is determined by multiplying the specific conductance by the total number of milliliters of solution containing one equivalent weight of the solute. The equivalent conductance is obtained for a normal solution when the specific conductance is multiplied by 1000, for a tenth-normal solution, when the specific conductance is multiplied by 10,000, and so on.

25 Change in Equivalent Conductance with Dilution

Let us start with one liter of a normal solution of hydrochloric acid, this liter is then diluted to two liters. If the total number of hydrogen and chloride ions remains the same, the number of ions in each milliliter of the more dilute solution is one half of the number in 1 ml. of the normal solution. Since the ions act as the carriers of the current, the specific conductance should be one half of its original value. When this specific conductance is multiplied by the number of milliliters (2000) that contains an equivalent weight of the solute, the equivalent conductance *should be the same* as it is for the normal solution. The equivalent conductance should not vary, therefore, with the dilution, *provided that the total number of ions does not change*. If this number should increase upon dilution, then the specific conductance would not be halved when the solution is diluted to two volumes, and the equivalent conductance would be greater for the half-normal solution than for the normal solution. Experimentally, we find that the equivalent conductance *does increase* with dilution. According to Arrhenius, this result must be interpreted as meaning that dilution causes a larger number of the molecules of the solute to form ions, the ionization of the electrolyte becomes more nearly complete as the solution is diluted. There is, however, another interpretation that can be placed upon the increase in equivalent conductance with the dilution, and this different point of view will be dis-

cussed in connection with the Debye-Huckel theory (page 413).

26 Measuring the Percentage of Ionization

As the dilution increases, a condition is finally reached when the equivalent conductance does not increase as more of the solvent is added. The degree of ionization of the electrolyte is then said to be 100 per cent, and the solution is said to be *infinitely dilute*. The equivalent conductance of an infinitely dilute solution is called the *limiting equivalent conductance* and corresponds, of course, to the maximum conductivity of all the ions that the solute can liberate. If the equivalent conductance of a solution of a finite concentration of the solute is 50 per cent of the limiting equivalent conductance (of the infinitely dilute solution) of the same solute, we may assume (according to the theory of Arrhenius) that this solution contains in all 50 per cent as many ions and is, therefore, 50 per cent ionized. This is one method of determining the degree of ionization of an electrolyte.

The degree of ionization of an electrolyte may also be determined from boiling and freezing-point data, this method has been discussed on page 404.

The apparent degrees of ionization of a number of acids, bases, and salts are shown in Table 23, page 437.

27 Conditions Which Influence the Degree of Ionization

Many of the conditions that influence the extent to which the same and different electrolytes are ionized in solution have been mentioned in various places in this chapter. These will now be briefly reviewed, and other conditions will be summarized.

(1) *Temperature* The effect of changes in temperature upon the apparent degree of ionization of highly ionized substances is very small. The effect upon the apparent ionization of weak electrolytes is more marked. The percentage of the ionized solute usually increases with increase in temperature, until a certain maximum is reached, and then decreases at higher temperatures.

(2) *The Nature of the Solute* The most highly ionized electrolytes in aqueous solutions are compounds of hydrogen or active metals with active non-metals or certain radicals. In general, we may say that electrovalent, or ionic, compounds are highly ionized electrolytes. Reactions between covalent compounds and the solvent, however, may produce a highly conducting solution. This is true, for example, for a solution of hydrogen chloride (page 155). Compounds in which atoms are united by covalences, if electrolytes at all, are weakly ionized. Since salts are, as a class, ionic compounds, they are all highly ionized. Acids and bases that are usually classed as "strong" are also highly ionized in aqueous solution.

(3) *The Effect of the Solvent* The part which the solvent plays in promoting the solubility and ionization of different solutes has been discussed on page 214. The apparent degree of ionization of most electrolytes is greater in water than in any other solvent. In general, the ionizing power of the solvent increases with increasing dielectric constant (page 214). No doubt the ability of the solvent to react with one or more of the ions of some substances has an important influence upon the production of ions.

(4) *Dilution* If we consider the ions of an electrolyte as existing in a state of equilibrium with undissociated molecules, the effect of dilution upon the apparent degree of ionization is easily understood. As the ions are scattered through a greater volume of solution, it becomes increasingly more difficult for them to recombine, because there are fewer meetings between ions of opposite charge. Hence, the number of ionic combinations that occurs per second is decreased, while the number of molecules that dissociate in the same period of time is unaffected by the dilution. This condition leads, therefore, to the production of more ions than are removed from the solution by the reverse reaction.

Experimental evidence bears out the above prediction which is based purely upon the kinetic theory. We have noted (page 411) that the equivalent conductance increases with dilution, and we have shown that this may be explained as the result of an increase in the relative number of molecules ionized. Freezing- and boiling-point data furnish evidence of the same character. As the concentration of a sodium chloride solution, for example, is decreased, the lowering of the

freezing point becomes nearer and nearer two times the lowering in a sugar solution of the same concentration.

SOME MODIFICATIONS OF THE THEORY OF IONIZATION

28. Objections to Arrhenius's Theory

In the preceding discussion, we have attempted to apply the essential points of Arrhenius's theory, as outlined on page 398, in explaining the properties of solutions of electrolytes. While the agreement between theory and facts is fairly satisfactory, on the whole, the student probably recognizes certain inconsistencies between this theory and the information that we now possess on such subjects as crystal structure, atomic structure, and the source of ionic charge — information that was not available to Arrhenius.

Thus, crystals of substances, such as sodium chloride, are shown by X-ray analyses of their structures to consist only of ions. Sodium chloride is completely ionized even before it is dissolved. When the crystal of sodium chloride dissolves in water, it does so because the molecules of the solvent weaken the attractive forces which exist between the ions in the crystal (page 214). There is no reason to believe that sodium and chloride ions combine in a solution to form molecules, since in solution, and in the fused state, the ions must be more nearly independent than they are in the crystal. In the crystal each ion appears to attract the ions of the opposite charge in all directions. As a result, a sodium ion, for example, occupies the center of a cube, and in the centers of the six faces of this cube there are six chloride ions. If molecules should form, when sodium chloride dissolves, we should have to conclude that the attraction of the sodium ion in solution is exerted in a single direction and hence that this ion combines with a single chloride ion. Such a conclusion would not appear to be logical. It is much more satisfactory to think of the ions in the

solution as attracting each other as they do in the crystal. The difference must consist in the strength rather than in the character of this attraction.

If we should assume, although there is no good reason for doing so, that molecules of sodium chloride exist in solution, we should have to explain our assumption by making a second assumption, namely, that the electrovalence of sodium chloride in the crystal changes, in solution, to covalence between some of the sodium and chloride ions. We should then be faced with the problem of explaining why this change does not happen for all of the sodium and chloride ions, if it is possible for it to occur for a certain percentage of them. If we are to retain our idea of the equilibrium between ions and molecules, then it becomes necessary to think of the electrovalence and covalence of sodium and chlorine as changing continuously from one to the other. As the water of the solution is removed by evaporation, or as the ions are crowded more closely together by any change in the solution that increases the concentration, the character of the compound becomes undoubtedly electrovalent, because the crystal state finally forms, and there can be no doubt as to the ionic, as opposed to the molecular, state of the solid. We should have to explain why covalence should not become more pronounced as the ions are crowded closer together and a greater number of collisions between them becomes possible.

It appears, therefore, that we must accept the conclusion that some strong electrolytes, such as sodium chloride, are 100 per cent ionized in aqueous solution. Now, then, shall we explain the apparent degrees of ionization that are frequently much less than 100 per cent as measured by electrical conductivity or by the effects of strong electrolytes upon the boiling and freezing points of the solvent? Arrhenius was certain that data of this kind could mean only that different percentages of the electrolyte molecules were ionized under different conditions.

29. The Debye-Huckel Theory of Strong Electrolytes

Our present ideas concerning solutions of strong electrolytes are in agreement with our information about the crystalline states of substances like sodium chloride. Most of these ideas are embodied in the *Debye-Huckel Theory*. Although this theory assumes that a strong electrolyte is 100 per cent ionized, the ions are not regarded as completely independent. Instead of thinking of two ions as combined in the form of a molecule, we think of ions as existing in the solution in somewhat the same condition as they exist in the crystal, i.e., *each ion attracts those of the opposite charge in all directions*. For this reason, the theory that we are now discussing is sometimes called the *Interionic Attraction Theory*. The attraction of ions for one another results in what we may consider as a field of the opposite kind of charge around each ion, that is, in the field surrounding an ion there will be more ions carrying the opposite charge than those carrying the same kind of charge. When an ion migrates toward one of the electrodes in a cell, the electrostatic attraction existing between it and the field around it must be overcome. This retards the mobility of the ion. An extreme case of the same sort exists in the crystalline state of the substance. Imagine a small crystal of sodium chloride, such as the one shown in Figure 194, between two terminals of a battery. The ion at the center has zero mobility since it is surrounded by six ions of the opposite kind, and these are urged by the potential between

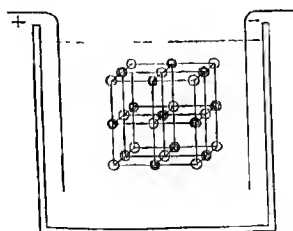


Figure 194

the electrodes to migrate in the opposite direction. In a large crystal every ion, except the relatively small number on the faces, is in the same situation as the ion at the center of the small cube. In a solution of sodium chloride, the crystal's structure, of course, has disappeared, but the attraction between oppositely charged ions still exists, although it is considerably weakened by the effect of the solvent (page 214). This attraction restricts the independent action, and particularly the movement, of the ions.

30 How the Theory Explains Apparent Percentages of Ionization of Strong Electrolytes

Now the conductivity of a solution depends upon the number of ions in the solution and upon the velocity with which they migrate toward the electrodes. If they did not move, they would never reach the electrodes, and regardless of the number that might be present, the conductivity would fall to zero as soon as those ions in contact with the electrodes were discharged. If the ions were absolutely independent of all forces that restrict their movement, the conductivity of the solution would be proportional to the number of ions in the solution. But if their migration is retarded or hindered in any way, the conductivity of the solution that contains them will be decreased by an amount which depends upon the extent that they do not act as independent particles.

Let us imagine, for convenience and simplicity, that a solution contains 100 ions each of sodium and chlorine in a definite volume. If these ions were entirely free of attraction in their solution environment, the solution would show a certain maximum conductivity. This would represent the condition which, in the Arrhenius theory, is called infinite dilution. But if these ions attract each other, and are retarded somewhat as they migrate toward their respective electrodes, the observed conductivity of the solution will be less than the maximum. Let

us say that it is 90 per cent of this maximum. In terms of Arrhenius's theory, we should say that the solute is only 90 per cent ionized, and that 10 per cent of the solute exists as undissociated molecules. In terms of the Debye-Huckel theory, we should say that 100 ions of each kind, which are restricted in action but which are free of all molecular combinations, produce the same observable conductivity as would be produced by 90 ions of each kind, if they were completely free and unobstructed in their individual actions.

The same restraining influences that ions in solution exert upon one another may account for the apparent degree of ionization of an electrolyte as measured by the freezing and boiling points, or the osmotic pressure, of its solution. Thus, a molal solution of sodium chloride may contain 6.02×10^{23} chloride ions and 6.02×10^{23} sodium ions. If these were absolutely free and unobstructed, the freezing point of the solution would be -3.72° . The fact that the freezing point of this solution is only -3.42° was taken to mean, by Arrhenius, that the electrolyte is only about 84 per cent ionized. But the effect of the solute in lowering the vapor tension of the solute, and hence in lowering the freezing point, depends not only upon the number of ions but upon their movement as well. To the extent that an ion in a solution is restrained in the freedom of its action, to that extent does it act as only a fraction of a free particle. Viewed in this light, 100 ions may be affected in such a manner by one another, and by their general environment in the solution, that they produce the ultimate effect on the properties of the solution of only 84 free particles.

We see, therefore, that it is possible to explain the measurements upon which apparent percentages of ionization are based without assuming that any portion of a strong electrolyte exists in solution as undissociated molecules. As the concentration of a solution of an electrolyte is increased, the ions are crowded closer together and they consequently exert greater attraction for one another. Finally, they assume their proper positions in the space lattice of the solid. As the concentration of the solution ap-

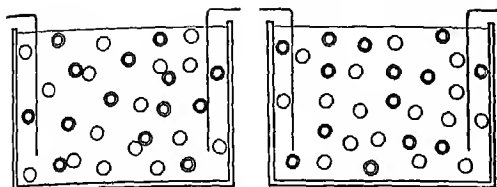


Figure 195. A Comparison of the Arrhenius Theory and the Theory of Debye and Huckel

In one case, the solution is assumed to contain both molecules and ions of the solute, in the other case, the solution is assumed to contain only ions

proaches the saturation point, we must think of the ions as becoming less and less independent. The equivalent conductance of the solution decreases, and the lowering of the freezing point and the elevation of the boiling point become more nearly the same as the effects of equal concentrations of a non-electrolyte. Likewise, the effect of dilution can be explained, not as due to the ionization of an increased number of molecules, but as due to the greater degree of freedom of action possessed by individual ions in the more dilute solution. Each ion acts more nearly as an individual and less as a portion of a combination.

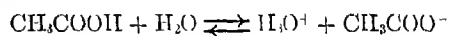
31 Ionization of Weak Electrolytes

The objections that may be raised against Arrhenius's theory apply, on the whole, only to solutions of strong electrolytes. For solutions of weak electrolytes it is still possible, and indeed necessary, to regard the undissociated molecules, as well as ions, as realities. The weak electrolytes are usually acids, such as acetic, or bases, such as ammonium hydroxide. A few substances usually classed as salts must be included, thus, mercuric chloride has a very small apparent degree of ionization in solutions of the usual concentration, and pure liquid aluminum chloride is a non-conductor of the current.

The structures of weak electrolytes are thought to depend, for the most part, upon covalence instead of electrovalence. At least in most of these compounds we may account for the production of ions by considering the possible reactions of the solvent

molecules with the molecules of the solute (page 155). It is probable that similar changes in solution are responsible, also, for the production of ions by some strong electrolytes. Hydrogen chloride, for example, in the pure state appears to be a typical covalent compound and is a non-conductor. In aqueous solution ionization may depend upon the reaction of molecules of water with the hydrogen of the acid to form the hydronium ion (H_3O^+) and chloride ion (page 155). This reaction must be almost complete, because hydrochloric acid shows about the same apparent degree of ionization as sodium chloride. However, it is entirely possible, and even probable, in the course of events in the solution that at least an occasional proton will leave the hydronium ion and recombine with the chloride ion by sharing a pair of electrons. In concentrated solutions of the acid this event becomes more than probable, it actually happens, as shown by the definite vapor pressure of the hydrogen chloride in these solutions.

In solutions of weaker acids, such as acetic, we may think of the following reversible reaction with the solvent as occurring



This reaction is by no means as complete as the reaction between HCl and water. In the latter, we may assume that the proton forms a much stronger covalent bond with the oxygen atom of water than with chlorine. In the acetic acid solution, we may assume that the covalent linkage between hydrogen and the oxygen atom of the acid is stronger than the bond between the proton and the oxygen atom of the water molecule.

Certain compounds that resemble salts of metals in some ways, e.g., aluminum chloride, AlCl_3 , and stannic chloride, SnCl_4 , are non-electrolytes in the liquid state. Their aqueous solutions, however, are good conductors. They must accordingly react with the solvent in a manner similar to the reaction of hydrogen chloride with water

to form ions. For aluminum chloride, this reaction is thought to be the following.



Other hydrates of the aluminum ion are probably formed at the same time.

There are relatively few ions in the solutions of weak electrolytes at ordinary concentrations. Hence, the attraction between ions is negligible, or almost so, and the effects which we observe for strong electrolytes, and which are explained upon the basis of interionic attraction, are correspondingly less pronounced. Arrhenius's theory holds very well for the solutions of these substances. In dealing with weak electrolytes, therefore, we shall follow the principles of that theory.

Review Exercises

1. Summarize the different kinds of evidence which show that salts, acids, and bases produce ions in aqueous solutions.
2. How many coulombs of electricity are required to deposit 53.94 g. of silver, 10 g. of copper, and 20 g. of antimony from solutions containing the ions of these metals?
3. A solution contains 60 g. of CaCl_2 in 1000 g. of water. If the degree of ionization of the salt is 75 per cent, what is the freezing point of the solution?
4. For what reason did Arrhenius assume that molecules of sodium chloride are in equilibrium with sodium and chloride ions in an aqueous solution of that substance?
5. We now believe that sodium chloride in an aqueous solution is completely ionized. If this is true, why does the conductivity method of measuring the degree of ionization show that this substance (in N/10 solution) is only 84 per cent ionized?
6. What data must be available for the calculation of the equivalent conductivity of a solution?
7. Define an infinitely dilute solution. Why does further dilution of an infinitely dilute solution not produce a change in the equivalent conductivity? Does dilution of such a solution affect the specific conductivity? Explain.

8. The equivalent conductances of acetic acid solutions of different concentrations are given below. Calculate the degree of ionization for each concentration.

10 N	0.05 reciprocal ohms
1 N	1.32 reciprocal ohms
0.1 N	4.6 reciprocal ohms
0.01 N	14.3 reciprocal ohms
Infinite dilution	352 reciprocal ohms

9. Compare the quantities of electricity required to deposit the same weight of iron from solutions containing ferrous and ferric ions.
10. Explain the meaning of the following statement: The acetic acid (HAc) in a tenth-normal solution is 1.3 per cent ionized. Calculate the concentration (in gram-ions or gram-molecules) of H^+ , Ac^- , and HAc in this solution.
11. Explain the effect of diluting a solution upon the equivalent conductivity of the solution in terms of (1) Arrhenius's theory and (2) the Debye-Huckel theory.
12. If acetic acid (N/10) is 1.3 per cent ionized, what weight of pure acetic acid and what volume of solution would be required to furnish one gram-ion of $\text{C}_2\text{H}_3\text{O}_2^-$ ion?
13. What is the principal difference between the theory of Arrhenius and that of Debye and Huckel as regards strong electrolytes?
14. The freezing point of a solution containing 4 grams of sodium hydroxide in 200 g. of water is -1.674° . What is the apparent percentage of ionization of the sodium hydroxide?
15. What should be the freezing point of a solution containing 0.1 of a gram-molecular weight (or formula weight) of sodium chloride in 1000 g. of water, if the sodium chloride is apparently 90 per cent ionized?
16. Explain the changes that occur at the electrodes during the electrolysis of a solution of hydrogen chloride in water.
17. Why is the reaction between ethyl alcohol and acetic acid slower than the reaction of sodium hydroxide and acetic acid?
18. Why can molecular or formula weights of electrolytes not be determined by the freezing or boiling-point methods?
19. The apparent percentage of ionization of cupric sulfate, CuSO_4 , is much smaller than that of sodium chloride. Both are completely

ionized according to the Debye-Huckel theory. Can you suggest an explanation?

20. What factors or conditions determine the quantity of electrical energy used in the electrolysis of a solution of a salt of a metal?
21. If no energy is required to separate the ions in a solution, thus dissociating molecules of the electrolyte, why are different decomposition voltages required to electrolyze different compounds?
22. For what purposes is electrical energy used in the electrolysis of a compound?
23. How can one account for the fact that acetic acid, or any other weak acid, is less ionized, in an aqueous solution, than hydrochloric acid?
24. Why is the assumption that *all* electrolytes are completely ionized in aqueous solutions not sound?

References for Further Reading

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CHEMICAL EQUILIBRIUM

Oxidation of CH_4 is more difficult than oxidation of CH_3OH . To obtain valuable relations in this field, an exact knowledge of reaction velocity is necessary, and I, therefore, went over to the study of reaction velocity and thus arose my "Etudes de Dynamique Chimique"

VAN'T HOFF

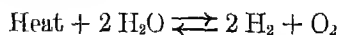
1 Introduction

We have employed frequently the general principle of equilibrium in describing the condition finally attained when two changes operating in opposite directions are allowed to occur simultaneously. It was necessary, for example, to make use of this principle in explaining Arrhenius's theory of ionization in the preceding chapter. Most of our examples of equilibrium, however, have dealt with physical rather than chemical changes; for example, we have defined a saturated solution as one in equilibrium with the undissolved solute. Chemical equilibrium, like physical equilibrium, requires that the two changes in opposite directions occur at the same speed, the principal difference is that in chemical equilibrium the two changes involve different substances.

Most reactions will attain a state of equilibrium unless they are prevented from doing so by the escape or removal of one or more of the substances involved. In some chemical changes the speeds of the forward and the reverse reactions become equal when only relatively small quantities of the original materials have been converted into the products; in such instances, the forward reactions (\longrightarrow) are far from complete, and some of them occur to such a small extent that products of the reaction cannot be de-

tected. In other changes, the forward reactions are almost complete — the starting materials are almost completely consumed — and the reverse reactions (\longleftarrow) are negligible in extent. In still others, the two reactions, forward and reverse, occur more nearly to the same extent, both the original substances and the products are present in considerable concentrations when equilibrium has been established.

Our usual intention in employing a reaction is to produce as much of the products from the starting materials as possible. It is evident, however, that the possibilities of a reaction are limited by the conditions of equilibrium for that reaction and the reaction that occurs in the opposite direction. Thus, the reaction



is apparently complete toward the left at ordinary temperatures although, theoretically at least, it is reversible at all temperatures. At 2000°C , equilibrium is reached when about 2 per cent of the water has decomposed into hydrogen and oxygen. Knowing the equilibrium conditions of this reaction, we should not select this method for the production of hydrogen and oxygen.

The equilibrium state of a reaction — that is, the relative concentrations, when the re-

action has reached equilibrium, of the products and the original substances — is not the same under all the conditions that may affect the reaction. The decomposition of water reaches equilibrium at 2000° when about 2 per cent has decomposed, but at 1000° only about 0.01 per cent decomposes before the reverse reaction occurs at the same speed as the decomposition. A knowledge of equilibrium states under different conditions is therefore of great importance, because by proper selection of conditions it is possible to produce much more of the products of the reaction.

A change in some conditions appears to influence the speed with which equilibrium is attained rather than the proportion of starting materials and products when equilibrium is reached. In any event, however, the conditions that influence the speed of a reaction are of considerable importance both in the laboratory and in industrial practice. They are also important in our understanding of many reactions that occur in nature.

When we speak of the speed of a reaction we refer to the mass of the reacting materials converted into the products of the reaction in a definite period of time. The rate of this conversion depends upon a number of factors.

2. The Nature of the Reacting Substances

Under the same conditions, two reactions involving different substances proceed at different rates, and the nature of the reacting substances has a great deal to do with the rate at which the reaction proceeds. Thus, at ordinary temperatures sodium and chlorine react much more rapidly than iron and chlorine. At one time it was said that sodium and chlorine have more "chemical affinity" for each other than iron and chlorine. It is evident, however, that a term so indefinite in meaning as "affinity" is only a name for a condition, and its use has now disappeared almost entirely from chemical literature. Instead, we explain differences in the tendencies of various substances to react

upon the basis of their atomic, ionic, or molecular structures. Thus, sodium reacts more readily with chlorine than iron does, because the sodium atom gives up its valence electron to chlorine more readily. In general, reactions between ions are very rapid and their speeds can be measured only with difficulty, if they can be measured at all. Reactions between molecules are often relatively slow and occur at speeds which can be measured without very great difficulty (page 400).

3. Temperature

The effect of changes in temperature upon the speed of chemical reactions has been discussed in a previous chapter (page 80). The same change in temperature affects the speed of most reactions in approximately the same manner. Roughly speaking, the speed is doubled for an increase of 10° , but for some reactions a similar change in temperature — let us say from 40° to 50° — more than doubles the speed.

To some extent the increase in speed with increasing temperature can be explained by the greater number of collisions between molecules that results from the greater velocity of the molecules at the higher temperatures, but this effect cannot explain all the change in speed. An increase in temperature of 10° does not, by any means, double the number of collisions, and hence, if this were the only factor involved, it should not double the speed of the reaction. Molecules that react must meet or collide, but mere collision does not always result in a reaction. At higher temperatures, the collisions are between molecules that are moving more rapidly and that consequently possess more kinetic energy. As compared to collisions between slowly moving molecules, such collisions may be expected to be more effective in breaking the bonds that hold together the atoms or radicals of the original substances, thus making possible other and more stable combinations of the same particles. Furthermore, as the temperature rises and energy

is absorbed, the electrons of atoms in the reacting substances may be shifted to higher energy levels. Atoms in which such changes occur may be expected to be more reactive, for example, this condition may easily lead to the breaking of a bond consisting of a pair of electrons that is shared by two atoms. Also, an electron considerably removed from the nucleus is more easily separated entirely than an electron that lies in its normal position, that is, in the lowest energy level. As the temperature rises, more molecules are *activated*, in other words, they possess the energy required to allow them to react when they collide with other molecules. For most reactions it appears, therefore, that a rise in temperature of 10° doubles the speed, because this change in temperature approximately doubles the number of activated molecules.

4 Catalytic Agents

The speeds of many reactions are greatly influenced by certain *catalysts*, which are not permanently affected during the chemical changes. Some catalysts accelerate and others retard the speeds of the reactions. A substance that catalyzes one reaction may have no effect upon another reaction. The speed of a reaction is often accelerated by means of a catalyst instead of an increase in the temperature. The latter not only may be more expensive than the use of a catalyst, but it may be actually undesirable, since many reactions are less complete at higher temperatures. Furthermore, the product that we want to make may be decomposed at a high temperature. When this is true, attempts to increase the speed by increasing the temperature may be successful in speeding up the reaction, but they will at the same time result in decreased yields and probably in the complete loss of the product. Under these conditions a catalyst is desirable. It is not believed that a catalyst changes the equilibrium condition of a reaction, hence, a reaction that occurs very slowly at low or moderately high temperatures, although it

may be fairly complete in the end, may be accelerated at the low temperature by using a suitable catalyst without decreasing the theoretical yield of the product. Since it does not affect the final equilibrium condition, a catalyst must exert equal effects upon the speeds of the forward and the reverse actions.

Control of the velocity of a reaction is often as important as, or even more important than, the maximum yield of the product which can be produced by that reaction. Even if the equilibrium conditions of a reaction permit the conversion of only ten per cent of one substance into another, the production of this small yield is usually more important and economical, if it can be produced in ten minutes, than the conversion of ninety per cent would be if this were accomplished in ten days.

The name *catalyst* was suggested by Berzelius in 1838. It signifies a substance which "loosens" the activities of certain substances and causes them to react more rapidly with other substances. The German chemist Wilhelm Ostwald compared a catalyst to a lubricant, which allows machinery to run more smoothly and more rapidly.

The action of a catalyst is sometimes obscure, and the usual definition of the term (page 68) does not explain the effect. We can be certain only that the catalyst is not finally changed into a different substance and that it gives up none of the chemical energy stored within it. Therefore, the catalyst does not alter the equilibrium state of the reaction. Some of the other features of catalysis may be summarized very briefly.

(1) The effect of the catalyst upon the speed of the reaction is almost always exceedingly great as compared with the quantity of the substance used to produce the effect. Thus, the small amounts of moisture which may remain in gases that have been dried as carefully and completely as possible may have decided influences upon the speed with which the gases enter reactions. Finely divided platinum in a suspended or colloidal state has a pronounced catalytic effect upon the decomposi-

tion of hydrogen peroxide, although the quantity of platinum present amounts only to one gram in 350,000 liters

(2) Sometimes the addition of a second substance may *promote* the catalytic activity of a catalyst which, when acting alone, has little effect. The potassium aluminate which is added along with iron in the catalysis of the reaction of nitrogen and hydrogen serves in this capacity in the production of ammonia.

(3) Some substances act as negative catalysts and decrease the velocity of a reaction. Acetanilide, for example, retards the decomposition of hydrogen peroxide. Water retards the decomposition of ammonia into nitrogen and hydrogen. Various substances are added to rubber articles to retard the deterioration that results from their slow oxidation. Sometimes it appears that the action of a negative catalyst may be explained as the action of one substance in repressing the positive catalytic influence of another. In such cases the negative catalysts may be regarded as "poisons." Finely divided platinum may be used to catalyze the oxidation of illuminating gas (page 113), this is the principle upon which some automatic gas lighters operate. After a time, the platinum loses its catalytic activity. This loss is probably due to the adsorption of certain substances which are present in the gas and which act as "poisons" to the catalyst.

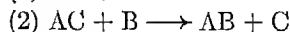
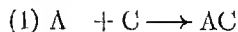
(4) Although a catalyst is not converted into any new substance during its period of activity, this does not mean that the catalyst remains unchanged in a physical sense. For example, a smooth platinum foil that is used as a catalyst in oxidizing ammonia to nitric acid, loses its smooth surface and becomes rough after considerable use.

5 An Explanation of the Effects of Some Catalysts

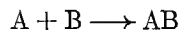
(1) Formation of Intermediate Compounds

In some reactions the catalyst appears to combine with one of the reacting substances to produce a compound which, in turn, reacts with the second substance to form the product and to liberate the catalyst. If C is the catalyst and A and B are the reacting substances, the mechanism of the reaction may be explained by the following equations

The reactions are assumed to occur in the order indicated



The speed with which the product AB is formed will be increased if the speed of the two reactions is greater than the speed of the simple reaction



The substance designated as C acts as a catalyst, therefore, by making possible certain intermediate reactions, which take place with a greater velocity, but which lead to the formation of the same product as the simple, uncatalyzed reaction. Although C takes part in the reaction, it is not converted ultimately into any new substance. Substances that act as C does in this hypothetical case are sometimes called *carrier catalysts*.

(2) *Contact Catalysts* The oxidation of alcohol may be catalyzed by the mere presence of a piece of platinum foil or wire. We may assume that this reaction is catalyzed only on the surface of the catalyst. Similar action is observed when a mixture of hydrogen and oxygen is exploded at ordinary temperature by finely divided platinum, when ammonia is oxidized to nitric acid in the presence of a platinum foil or gauze, when liquid fats are converted into solids by hydrogen in the presence of finely divided nickel, and in other reactions, many of which are of considerable industrial importance. Substances that influence the speeds of reaction in this manner are said to act as *contact catalysts*. In the action of these substances,

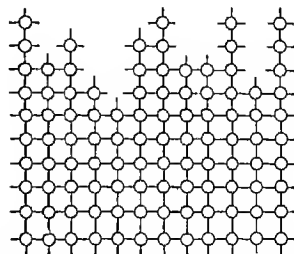


Figure 196 The Surface of a Crystal of Nickel

it is probable that the catalytic effect depends upon increases in the concentrations of the reacting substances. The concentrations are increased by the action of the catalyst in *adsorbing the reacting substances upon its surface*. As might be expected, therefore, the effect is increased when finely divided solids are used rather than larger masses, because for a definite weight of material the amount of surface increases greatly as the particles are reduced to smaller and smaller dimensions.

Adsorption by the catalyst may depend upon the irregular arrangement of atoms upon its surface; Figure 196 shows the condition of the surface of a crystal of nickel. If we could examine the minute details of the surface of such a crystal, we should probably find that it is not smooth, but that it consists of numerous "hills" and "valleys" because of the irregular spacing of its surface atoms. The atoms in the body of the crystal are attracted equally in all directions, but the atoms on the surface, especially those in the "valleys" and along the sides of the "hills," have free attractions by means of which they may be able to hold particles — atoms, molecules, or ions — of the substances participating in the reaction that the crystal catalyzes in much the same manner as they attract atoms of their own kind. In some instances, the attraction may be sufficiently great to split molecules, such as O_2 and H_2 , allowing single atoms of the elements to be adsorbed. If this happens, the subsequent reaction that occurs between *atoms* of hydrogen and oxygen might be expected to occur more rapidly than the reaction between undissociated molecules of the two elements. Furthermore, the speed of the reaction should also be increased, because the adsorption of the two elements amounts to an increase in their concentrations, more of the molecules — or atoms — are crowded into a small space on the surface of the crystal than are present in the same space when it is occupied by the two gases under normal conditions.

6 The Effect of Concentration upon the Speed of a Reaction

Reactions occur between particles — atoms, molecules, or ions — and the speed of a reaction depends to some extent, therefore, upon the number of collisions between particles of different kinds in a definite period of time. The number of collisions depends, in turn, upon the number of each kind of particle in a given volume and upon the velocities of the particles. The greater the number of ions or molecules within a given space, the greater will be the speed of the reaction. For gases, the concentration increases with the pressure, hence reactions that involve substances in this state occur more rapidly under increased pressure. It is for this reason that pure oxygen reacts more vigorously in oxidation than air under the same pressure, only about one fifth of the air consists of the active element, and its partial pressure is one fifth of the total pressure.

7 The Law of Mass Action

The effect of concentration upon the speed of a reaction was stated by Guldberg and Waage, in 1867, as a general principle now called the Law of Mass Action. *The speed of a reaction is proportional to the active mass — or concentration — of each substance that takes part in the reaction.* Concentration is expressed, usually, as the number of gram-molecular weights of each substance in one liter.

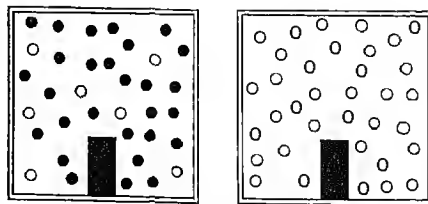
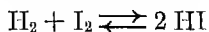


Figure 197 The Effect of the Concentration of Oxygen upon the Rate at Which a Substance is Oxidized

In air (left) only one fifth of the molecules surrounding the oxidizable substance are molecules of oxygen, in the other case, all the molecules are capable of supporting oxidation.

8 Derivation of a Mathematical Statement of the Law of Mass Action

Let us consider the reaction of hydrogen and iodine (vapor) to form hydrogen iodide



At a sufficiently high temperature, both hydrogen iodide and iodine—as well as hydrogen, of course—are gases. Although this reaction is reversible, we shall speak at present of only the forward reaction, the one producing HI.

The speed of this reaction, at constant temperature and at any one instant, is proportional to the number of hydrogen molecules in a definite volume—let us say in one liter, it is also proportional to the number of iodine molecules in the same volume. (The number of molecules per liter—the concentration—is expressed in terms of the number of gram-molecular weights per liter.) Let us represent the concentration of hydrogen as $[\text{H}_2]$ and that of iodine as $[\text{I}_2]$. Since the speed of the reaction is proportional to each of these quantities, it is proportional, also, to their product, $[\text{H}_2] \times [\text{I}_2]$, as long as conditions other than concentration are not changed. The speed depends, of course, upon the temperature, upon the presence of certain catalysts, and upon the characteristics of the reacting substances, but these are conditions that either are, or can be kept, constant.

Let us now represent the speed of the reaction between hydrogen and iodine, at some fixed temperature, under constant conditions as regards catalysts, and when the concentration of each of the reactants is one gram-molecular weight per liter, by the symbol K . This is called the *velocity constant* of the reaction at the fixed temperature. When $[\text{H}_2] = 1$ and $[\text{I}_2] = 1$, the speed, S , of the reaction is expressed as

$$S = 1 \times 1 \times K.$$

For other concentrations of hydrogen and iodine, the speed of the reaction is expressed as

$$S = K \times [\text{H}_2] \times [\text{I}_2]$$

Thus, if K is the speed when the concentration of hydrogen and iodine each is 1, the speed when $[\text{H}_2] = 2$ and $[\text{I}_2] = 3$ is

$$S = 2 \times 3 \times K = 6K$$

The increase in speed with increase in concentration can be understood with the help of Figure 198, in which we represent concentration by the number of molecules in a definite volume, there are two molecules of hydrogen in the second reaction for each molecule in the first. If the number of molecules of iodine remains unchanged, the number of chances that a hydrogen molecule will meet an iodine molecule and that the reaction producing hydrogen iodide will occur is twice as great as the number of chances that these events will occur when the concentration of hydrogen is 1. If the number of molecules of iodine per unit of volume is doubled, when the number of hydrogen molecules is doubled, the number of chances that one molecule of hydrogen will meet and react with one molecule of iodine is six times as great as it is when $[\text{H}_2]$ and $[\text{I}_2]$ are each 1.

9. Reactions Involving More than One Molecule of a Reactant

If more than one molecule of a reacting substance, as shown in the balanced equation for the reaction, takes part in a reaction, *the concentration of that substance must be used as many times in the equation for the speed of the reaction as there are molecules of the substance in the balanced equation for the reaction.*

Let us consider the reaction of nitric oxide and oxygen to form nitrogen dioxide

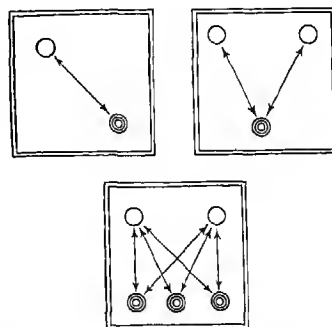
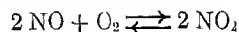


Figure 198 The Effects Produced upon the Speed of a Reaction by Changes in Concentration

The speed of this reaction cannot be expressed by the simple equation

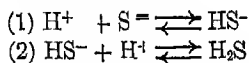
$$S = K \times [\text{NO}] \times [\text{O}_2]$$

This equation expresses the speed with which one molecule of oxygen reacts with one molecule of nitric oxide, whereas the actual equation requires one molecule of oxygen to react with two of nitric oxide. Hence, the speed of the reaction is not proportional to the simple product $[\text{NO}] \times [\text{O}_2]$, but to the product $[\text{NO}]^2 \times [\text{O}_2]$, and the equation for the speed is

$$S = K \times [\text{NO}]^2 \times [\text{O}_2].$$

The student will understand, of course, that K has different values for the two reactions which we have discussed. Even though the temperature be the same in all cases, K will have different values because we are using different reacting substances in the two cases.

The reason for squaring the quantity $[\text{NO}]$ in the equation above can be explained by reference to a similar and somewhat simpler reaction. Let us consider the reaction of hydrogen and sulfide ions to form, first, the hydrosulfide ion (HS^-), and then the molecule of H_2S .



The speed with which reaction (1) proceeds is expressed as

$$S_1 = K_1 \times [\text{H}^+] \times [\text{S}^-],$$

but this reaction leads only to the formation of the ion HS^- . To form a molecule of H_2S , the HS^- ion must react with a second hydrogen ion (equation 2). Evidently, the speed (S_2) of reaction (2) depends upon the speed with which the HS^- ion is formed by reaction (1). The speed (S_1) of reaction (1) is proportional to $[\text{H}^+] \times [\text{S}^-]$ and, therefore, the concentration of HS^- is also proportional to $[\text{H}^+] \times [\text{S}^-]$. Let us, therefore, substitute this product for $[\text{HS}^-]$ in the equation

$$S_2 = K_2 \times [\text{HS}^-] \times [\text{H}^+],$$

whereupon we obtain the equation

$$\begin{aligned} S_3 &= K_3 \times [\text{H}^+] \times [\text{H}^+] \times [\text{S}^-] \quad \text{or} \\ S_3 &= K_2 \times [\text{H}^+]^2 \times [\text{S}^-] \end{aligned}$$

for the speed (S_3) of the reaction that results in the formation of hydrogen sulfide molecules from the two ions.

EQUILIBRIUM

10. Reversible Reactions

Many reactions are reversible; that is, under suitable conditions the products of a given reaction will take part in a reverse reaction to form the starting materials. Reversible reactions to which we have referred in preceding chapters include (1) the oxidation of iron and the liberation of hydrogen in the reaction of steam and hot iron (page 109), (2) the oxidation of hydrogen chloride by oxygen (Deacon's process, page 327), (3) the formation of hydrogen chloride and sodium bisulfate by the reaction of salt and sulfuric acid in solution (page 346), (4) the conversion of sodium bicarbonate into sodium carbonate, water, and carbon dioxide (page 384); (5) the combination of hydrogen and oxygen to form water (page 418); and many others. In each of the reactions mentioned certain conditions favor one of the two reactions and other conditions favor the other. Thus, iron can be converted completely into iron oxide if the hydrogen produced by the reaction is removed completely, as it is formed, by a constant stream of steam. But if hydrogen is passed continuously over the heated oxide, the reverse reaction is completed, and the oxide is converted into iron and water; under these conditions the forward reaction has little chance to take place, because the steam is swept out of the reaction vessel by the stream of hydrogen, which is used, of course, in excess. In the formation of water from hydrogen and oxygen, the forward reaction is more nearly complete at 1000° than at 3000° , because the higher temperature favors the decomposition of water.

11. Irreversible Reactions

Some reactions appear to go to completion in one direction. Thus, there is no evidence that the oxygen and potassium chloride formed when potassium chlorate decomposes recombine directly to form the original substance under any conditions. Similarly, no conditions have ever been found favorable

for the recombination of the water and carbon produced when sugar is heated. It is now thought, however, that all reactions (theoretically, at least) are reversible if the proper conditions for the reverse reaction can be established.

12 The Equilibrium Constant

We shall now proceed to derive a mathematical equation showing the relation between the concentrations, at equilibrium, of all the substances that take part in a reversible reaction. As we derive and use this equation, we must keep in mind the following considerations:

(1) All the factors that influence the speeds of reaction are kept constant except concentration.

(2) All concentrations must be expressed in terms of the number of gram-molecular weights of the reacting substance in a definite volume (usually the liter). These concentrations, if not stated, can be calculated by dividing the weight of the substance (expressed as grams per liter) by the molecular weight of that substance. Thus, the concentration of a liter of oxygen which weighs 2 grams (the weight of a liter will depend upon the temperature and pressure at which the liter is measured) is $2/32 = 0.0625$ gram-molecular weight per liter. A solution containing 80 grams of hydrochloric acid per liter has a molecular concentration of $80/36.47 = 2.18$ gram-molecular weights per liter.

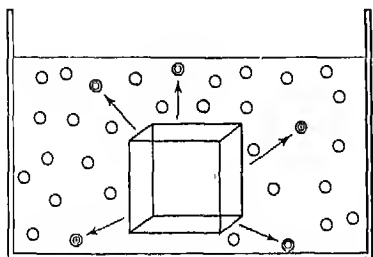
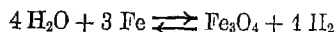


Figure 199 In a Reaction Involving Solids and Liquids and Gases, the Concentrations of the Solid Materials are Constant

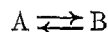
In the reaction between a gas and a solid, for example, it is assumed that the reaction actually occurs between the gas and the gaseous state of the solid. The active concentration of the solid is, therefore, proportional to its vapor pressure, which at a constant temperature, is constant as long as any of the solid remains.

(3) The concentrations of all undissolved solids which take part in a reaction may be considered as constant. Consider the reaction between steam and iron:



The speed of the forward reaction evidently depends upon the concentration of the steam, because all of its molecules are free to take part in this reaction, if they can come into contact with atoms of iron. We must assume that the atoms of iron that react are mixed with steam molecules and that, in fact, the reacting iron is in the gaseous state. The concentration of iron in this state is proportional to iron's vapor pressure, which for a definite temperature is constant as long as any of the iron remains. The concentration of iron, therefore, is also constant. It would be quite incorrect to consider that the speed of the reaction is proportional to the total quantity of iron in a definite volume. Hence we must consider the solid's concentration as constant during the reaction.

Let us now consider the hypothetical reaction in which molecules of substance A change into molecules of substance B. We shall think of the reaction as reversible, i.e., molecules of B also change into molecules of A.



We assume that one molecule of A produces one molecule of B. The speed (S_1) of the forward reaction, $\text{A} \rightarrow$, at equilibrium is expressed as

$$S_1 = [\text{A}] \times K_1,$$

where $[\text{A}]$ is the molecular concentration of A, and K_1 is the velocity constant that expresses the rate at which A changes into B when $[\text{A}]$ is one gram-molecular weight per liter. The speed, S_2 , of the reverse reaction at equilibrium is expressed as

$$S_2 = [\text{B}] \times K_2,$$

where K_2 is the velocity constant of this reaction and is different, of course, from K_1 . We understand that $[\text{A}]$ and $[\text{B}]$ represent the concentrations of A and B at equilibrium,

[A] does not represent the concentration of A at the beginning of the reaction.

At equilibrium,

$$S_1 = S_2$$

Hence, it is also true that

$$[A] \times K_1 = [B] \times K_2$$

Dividing each side of this equation by $[A] \times K_2$, we obtain

$$\frac{K_1}{K_2} = \frac{[B]}{[A]} = K_e$$

Since K_1 and K_2 are constants, K_1/K_2 or K_e is also a constant, we call K_e the *equilibrium constant* of the reaction

Starting with a definite concentration of A and zero concentration of [B], the forward reaction proceeds to produce molecules of B and to decrease the concentration of A. As soon as any B molecules are produced, they begin to change back into A molecules. The speed of the reverse reaction is very slow in the beginning because of the small number of B molecules, but more of these molecules are produced, and the speed of the reverse reaction increases, as the forward reaction continues. Meantime, the speed of the forward reaction is decreasing, because molecules of A are being consumed in this reaction. Eventually, the speeds of the two reactions become equal. Regardless of the concentration or total quantity of A with which we start the reaction, [A] will continue to decrease and [B] to increase until

$$\frac{[B]}{[A]} = K_e$$

If K_e is 1, A will change into B until the molecular concentrations of the two substances are the same

If the speed of the forward reaction is twice that of the reverse, for *equal concentrations* of A and B, it is evident that the two speeds will be equal and that equilibrium will result only when the number of molecules of B in a definite volume of the mixture is twice the number of molecules

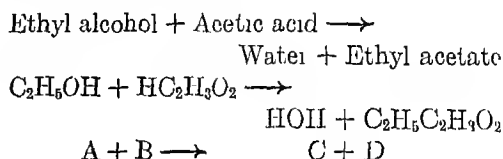
of A. In this event, the equilibrium constant for the reaction is

$$\frac{[B]}{[A]} = \frac{2}{1} = 2$$

If we could determine the relative speeds of the forward and reverse reactions for equal concentrations of the substances involved in the reactions, it would be easy from these values to determine the equilibrium constant. But the speeds of most reactions are difficult and often impossible to determine. Instead, we must determine the concentrations of the substances in the equilibrium mixture by experiments of different kinds, and from these values we calculate the value of K_e for the reaction in which the substances participate

13 The Equilibrium Equation for the Reaction $A + B \rightleftharpoons C + D$

Let us now consider the equation for the equilibrium constant of a reaction in which two substances, which we shall designate as A and B, change into two other substances, which we shall designate as C and D. If the reader desires a specific example of such a reaction, he may substitute for the general equation the following



Using the symbols [A] and [B] to represent the concentrations of A and B, as before, we may write the equation for the speed (S_1) of the forward reaction as

$$S_1 = [A] \times [B] \times K_1$$

The velocity constant K_1 , as before, expresses the speed with which the reaction proceeds, under a constant set of conditions as regards temperature, catalysts, and so on, when [A] and [B] are each one gram-molecular weight per liter. The speed (S_2) of the reverse reaction, $C + D \longrightarrow$, is expressed as

$$S_2 = [C] \times [D] \times K_2$$

At equilibrium, $S_1 = S_2$

Hence,

$$[A] \times [B] \times K_1 = [C] \times [D] \times K_2$$

Dividing each side of this equation by

$$[A] \times [B] \times K_2$$

we obtain:

$$\frac{K_1}{K_2} = \frac{[C] \times [D]}{[A] \times [B]}$$

As before, K_1/K_2 will be designated as K_e , the equilibrium constant

$$K_e = \frac{[C] \times [D]}{[A] \times [B]}$$

The equilibrium constant, K_e , as defined in the above equation is a number. It may be found by analyzing the equilibrium mixture and determining from the results of the analysis the molecular concentrations of A, B, C, and D. Knowing the molecular quantities (as shown by the equation) of the substances that are involved in the reaction, and knowing the concentrations of A and B in the beginning, it is usually sufficient to find by analysis the equilibrium concentration of a single substance in the reaction mixture.

If three gram-molecular weights of A and two of B, per liter, are added at the beginning of the reaction, and if, when equilibrium has been reached, one gram-molecular weight per liter of C has been formed, it is easy to see that the concentrations of the four substances are

[A] = 2 gram-molecular weights per liter

[B] = 1 gram-molecular weight per liter

[C] = 1 gram-molecular weight per liter

[D] = 1 gram-molecular weight per liter,

since one molecule of A reacts with one of B to form one of C and one of D. Under the conditions that result in the state of equilibrium that we have described, the value of K_e is

$$\frac{1 \times 1}{2 \times 1} = \frac{[C] \times [D]}{[A] \times [B]} = K_e = \frac{1}{2} \text{ or } 0.5.$$

14. The Meaning and Use of the Equilibrium Constant

Stated in words, the equilibrium equation has the following meaning. When a reversible

reaction (of the type $A + B \rightleftharpoons C + D$) has reached equilibrium, the ratio of the product of the concentrations of the substances formed to the product of the concentrations of the original substances has a definite numerical value. The value of this ratio is quite independent of the original concentrations of the reacting substances. It does vary, however, with certain conditions, such as temperature. The reaction has reached equilibrium only when the definite value of this ratio has been attained, and until this condition is fulfilled, the reaction is proceeding in the direction that will establish the required value.

The value of K_e for a given reaction is important, because it shows the extent to which the reacting substances are converted into the products of the reaction. A large value for K_e denotes a reaction in which relatively large portions of the reactants are changed into the products of the reaction, while a small value of K_e shows that the forward reaction occurs only slightly before equilibrium is reached. Information concerning the values of K_e under different conditions, such as different temperatures, is often of extreme importance. If these values are known, the conditions most favorable to the reaction in which we are interested can be selected.

15. The Equilibrium Equation for the Reaction $2A + B \longrightarrow C + D$

For reactions in which more than one molecule of a substance is involved the equilibrium equation takes a slightly different form. The modification involves, however, only the concentrations of the reacting substances. For the reaction $2A + B \longrightarrow$, we have shown (page 423) that the speed (S_1) is expressed by the equation

$$S_1 = [A]^2 \times [B] \times K_1$$

The speed (S_2) of the reverse reaction $C + D \longrightarrow$ is expressed by the equation,

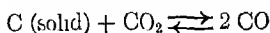
$$S_2 = [C] \times [D] \times K_2$$

Hence, the equilibrium constant for the reaction $2A + B \rightleftharpoons C + D$ is given by the equation

$$K_e = \frac{[C] \times [D]}{[A]^2 \times [B]}$$

16. Problems Based upon the Principle of the Equilibrium Equation

(a) The production of producer gas depends upon the reduction of carbon dioxide by carbon



The equilibrium mixture at one atmosphere and a temperature of 1123° contains 93.77 per cent (by volume) of carbon monoxide and 6.23 per cent of carbon dioxide. The equilibrium constant of the reaction is given by the equation:

$$K_e = \frac{[CO]^2}{[CO_2]}$$

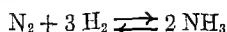
Now the concentrations of the two oxides are proportional to their partial pressures and, therefore, the equation for the equilibrium constant can be written as

$$K_e = \frac{p_{CO}^2}{p_{CO_2}}$$

The partial pressures of the two gases are in the same ratio as the relative quantities — or the number of molecules — of the two gases in a definite volume of the mixture. Therefore,

$$K_e = \frac{(0.9377)^2}{0.0623} = 14.11 \text{ atms.}$$

(b) The production of ammonia by the direct combination of hydrogen and nitrogen is one of the important reactions that is used to "fix" the nitrogen in the atmosphere as valuable and useful compounds



The composition of the equilibrium mixture of the three gases at 400° is as follows: ammonia 10.2 per cent (by volume), nitrogen 22.45 per cent, and hydrogen 67.35 per cent. What is the equilibrium constant for the reaction at the given temperature and a total pressure of 100 atms.?

Substituting the partial pressures, once more,

for the concentrations, the equilibrium constant is given by the equation

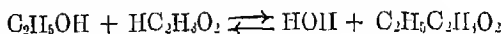
$$K_e = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3}$$

The partial pressure of ammonia is 10.2×100 atms, p_{H_2} is 67.35×100 atms, and p_{N_2} is 22.45×100 atms

Hence,

$$K_e = \frac{(10.2)^2}{22.45 \times (67.35)^3} = 1.5 \times 10^{-6} \text{ atm}$$

(c) Let us consider the reaction between ethyl alcohol (C_2H_5OH) and acetic acid ($HC_2H_3O_2$) to form water and ethyl acetate ($C_2H_5C_2H_3O_2$).



The equilibrium constant of this reaction is given by the equation

$$K_e = \frac{[C_2H_5C_2H_3O_2] \times [HOH]}{[C_2H_5OH] \times [HC_2H_3O_2]}$$

The speed with which this reaction proceeds may be followed by determining the concentration of acetic acid at different time intervals in equal samples of the mixture. If equal molecular concentrations of acid and alcohol are mixed in the beginning, it will be found, at equilibrium, that two thirds of each gram-molecule (per liter) of the acid has been converted into ethyl acetate and water at a temperature of 10° . What is the equilibrium constant of the reaction?

The concentrations of acid and alcohol in the beginning were equal, and two thirds of each gram-molecule of the acid and, of course, an equivalent weight of the alcohol are converted into ethyl acetate and water. Thus leaves, therefore, one third of a gram-molecule each of the acid and the alcohol, and two thirds of a gram-molecule each of water and ethyl acetate are produced. Substituting these values in the equilibrium equation,

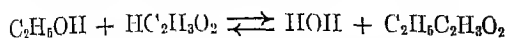
$$\frac{2/3 \times 2/3}{1/3 \times 1/3} = K_e = \frac{4/9}{1/9} = 4 \text{ (approximate)}$$

FACTORS THAT DISTURB EQUILIBRIUM

17. The Effect of Changes in Concentration

What will be the effect upon a reaction at equilibrium of adding or removing one of

the substances that participates in the reaction? Let us consider that the reaction



is at equilibrium. The concentration of the four substances, therefore, must be such that the equilibrium equation is satisfied

$$\frac{[H_2O] \times [C_2H_5C_2H_3O_2]}{[C_2H_5OH] \times [HC_2H_3O_2]} = K_e$$

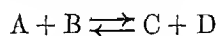
This equilibrium is disturbed when some of the water, for example, is removed from the mixture by adding some substance which reacts with water but with no other substance in the mixture. The removal of water causes the ratio of the products of the concentrations to be smaller, for the time at least, than the equilibrium constant K_e . Hence the reaction must adjust in such a manner that the value of K_e will be restored. If this is to happen, the concentrations of alcohol and acetic acid must become smaller, and those of water and ethyl acetate must become larger, until the ratio has again attained the same value as K_e ; this means, of course, that the forward reaction becomes more nearly complete as water, one of the products, is removed.

The effect of increasing the concentration of water is directly opposite to the effect of its removal. When water is added, the ratio will be larger, temporarily, than the equilibrium constant. In adjusting to re-establish equilibrium, the reaction produces alcohol and acetic acid more rapidly than they are consumed by the forward reaction, until the product of their concentrations divided into the product of the concentrations of water and ethyl acetate is again equal to the same value as before. When equilibrium is re-established, the concentration of ethyl acetate will be smaller than it was before more water was added, the concentrations of alcohol and acid will be greater.

As shown above, it is possible to convert one substance more nearly completely into the products of a reaction by increasing the concentration of the substance that reacts

with it. More ethyl acetate can be converted into ethyl alcohol and acetic acid by increasing the concentration of water. Similarly, more alcohol can be converted into water and ethyl acetate if a large excess of acetic acid is used. The same result is accomplished, also, by removing the water as it is formed.

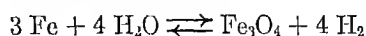
The principle just described — the effect of changes in concentration upon the equilibrium of a reaction — is frequently of great importance and value. Let us assume, for example, that in the reaction



A is a costly substance and B is relatively inexpensive. Without changing other conditions, such as the temperature, it is possible to convert a definite quantity of A into C and D more nearly completely if we use several times the theoretically required concentration of B, which is one molecule of B for each molecule of A. In this manner the chemist can control to some extent the concentrations of the substances that take part in, or are produced by, a reaction, although he does not change the equilibrium constant of the reaction.

18 Le Chatelier's Principle

The effect of changes in concentration upon chemical equilibrium is one illustration of an important generalization called the Principle of Le Chatelier. This principle states that *a reaction at equilibrium will adjust itself in such a way as to counteract and relieve the effect of any force or stress that disturbs the equilibrium state*. Thus, a change in the concentration of hydrogen in the following reaction may be regarded as a stress that disturbs the equilibrium

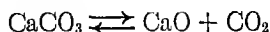


In overcoming or counteracting the effect of this stress, iron and steam will react more nearly completely, if hydrogen is allowed to escape or is removed. On the other hand, they are consumed to a smaller extent if

the reacting system is placed in a closed container and hydrogen is forced into the vessel under pressure, so that its concentration is increased. Stresses may also be produced by changes in temperature and pressure, but a change in the latter is a stress only if the reacting substances, or at least one of them, are gases.

19. Effect of Changes in Pressure upon Equilibrium

In the reaction



the only gaseous substance participating is carbon dioxide, solid calcium carbonate decomposes into the oxide, which is a solid, and the dioxide. Since the concentrations of both solids can be regarded as constant, the equilibrium constant for this reaction may be written as

$$[\text{CO}_2] = K_e$$

This equation signifies that the concentration of carbon dioxide, in equilibrium with both the carbonate and the oxide, at a definite temperature, is constant, since the concentration of carbon dioxide is proportional to its pressure, the pressure of the carbon dioxide in equilibrium with the two solids is also constant. If the pressure of the gas were increased beyond the constant equilibrium pressure, the reaction would adjust to restore equilibrium; hence, the reaction to the left would occur more rapidly than that to the right, until only sufficient carbon dioxide remained to establish the pressure — and hence the concentration — required for equilibrium. This pressure is the same, if the temperature remains constant, as it was before the equilibrium was disturbed and is independent of the total weight of carbonate or oxide involved. Therefore, since

$$[\text{CO}_2] = K_e,$$

the value of the equilibrium constant is not affected by the change in pressure. It should be noted, however, that an increase in the

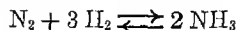
pressure of the gas does result in the production of less calcium oxide than would be possible if the pressure were allowed to remain at its lower value.

As a general rule we can state that the effect of an increase in pressure upon reactions in which gases are involved is to shift equilibrium in the direction of the substances represented in the equation for the reaction by the smaller total number of molecules of gases. In the decomposition of calcium carbonate, for example, an increase in the pressure of carbon dioxide shifts the equilibrium in the direction of calcium carbonate, thus reducing the number of carbon dioxide molecules per unit of volume. The stress produced by the increased pressure is thus relieved in keeping with Le Chatelier's principle, because the increase in pressure is counteracted by a decrease in the number of molecules, a change that *lowers* the pressure.

Since changes in pressure can be interpreted as changes in concentrations of gases, the effect of pressure changes can be regarded as a special case of the disturbance of equilibrium caused by changes in concentration.

20 Two Examples of the Effect of Pressure upon Reactions

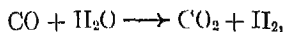
Let us refer once again to the reaction (page 428) by which ammonia is produced from nitrogen and hydrogen



The equation shows that *two* molecules of ammonia are produced from one molecule of nitrogen and three of hydrogen, or from four molecules in all. If a mixture containing these three gases in equilibrium is subjected to an increase in pressure, the concentration of ammonia will be increased, and the concentrations of nitrogen and hydrogen will be decreased. This effect is in keeping with Le Chatelier's principle because, if the volume and temperature are unchanged, two molecules of ammonia will exert less pressure than four molecules in all of hydrogen and nitrogen, the only way in which the increase in pressure can be counteracted is by reducing the number of molecules that exert the pressure, and

this is the result when nitrogen and hydrogen are converted into ammonia. To produce ammonia by this reaction a relatively high pressure, therefore, is desirable

In the reaction of carbon monoxide with water vapor,



there is no change in the total number of molecules per unit of volume as the reaction occurs — two molecules are produced from two molecules. Hence a change in pressure has no effect upon the relative concentrations of the four substances, the yield of hydrogen cannot be increased by either an increase or a decrease of pressure

21. Effect of Changes in Temperature

The temperature of a system rises or falls as heat is added or removed. When the system is undergoing a chemical change, heat may be added to it for two reasons: (1) To raise the temperature in order that the velocity of the reaction may be increased, and (2) to change the equilibrium constant so that a greater yield of the substance that we desire to produce may be obtained. The first of these effects, the increase in velocity, has already been discussed (page 419). Many reactions proceed almost to completion before equilibrium is established, but the velocity of the forward reaction may be so slow that the product is not formed rapidly enough to allow the reaction to be used commercially. In that event, the reaction may be speeded up and more of the product may be formed in a given period of time by increasing the temperature.

In considering the desirability of applying heat to raise the temperature, we must bear in mind, however, the effect of heat upon the equilibrium of the reaction. The addition of heat constitutes a "stress" in the sense in which that term is used in Le Chatelier's principle. Accordingly, the equilibrium will be shifted in the direction in which that stress is relieved. When heat is applied, this means that the reaction in which heat is absorbed will be favored.

22. Two Examples Showing the Effect of Temperature Changes

Let us consider again the reaction

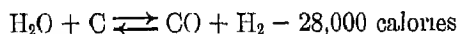


When two gram-molecular weights of ammonia are produced from nitrogen and hydrogen, 22,000 calories of heat are liberated. A like quantity of heat is absorbed when the reverse reaction takes place, and two gram-molecular weights of ammonia are decomposed into the elements. As long as the reaction is at equilibrium, the heat liberated by the forward reaction is absorbed by the reverse reaction, since the two are occurring at equal velocities. If heat is added from an outside source, the reaction that absorbs heat will be favored, that is, the substance or substances that require absorption of heat when they are made will be produced in larger quantities, and their concentrations will be increased, while the concentrations of the substances that produce them will be decreased. If the reaction is carried out under conditions in which heat is removed, the temperature will be kept at a lower value, and equilibrium will be shifted toward the completion of the reaction that evolves heat. The point of equilibrium cannot be shifted in this manner, however, without changing the value of the equilibrium constant, *which has a different value for each temperature*.

From a consideration of the above principles it is evident that the reaction of hydrogen and nitrogen should be carried out at relatively low temperatures, if it is to be used to produce ammonia commercially. At low temperatures, however, the velocity of the reaction is undesirably slow. For a definite temperature, the yield of ammonia can be increased considerably by increasing the pressure, but the reaction occurs at a very slow rate. If the reaction is operated at a very high temperature, the velocity may be increased but only at the cost of cutting down the yield to a point where the reaction is of little practical value. The only solution to the problem, therefore, is to find some catalyst that will

increase the velocity of the reaction at temperatures that do not seriously shift the equilibrium in the wrong direction. The reaction is used commercially to produce ammonia. The operating conditions consist of a temperature around 500°C and a pressure of 200–1000 atmospheres. To increase the speed at this temperature several different catalysts have been employed. One of the most effective catalysts is a mixture of finely divided iron and two oxides, of which one must be basic and the other acid. The two oxides sometimes used are K_2O and Al_2O_3 , which, combined, form potassium aluminate.

Let us also consider the effect of increasing the temperature upon the reaction used to produce water gas

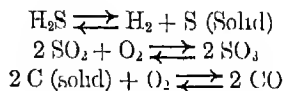


The mixture of carbon monoxide and hydrogen is produced from steam and carbon only as heat is absorbed. In accordance with Le Chatelier's principle, the application of heat will favor the reaction producing hydrogen and carbon monoxide, because this reaction requires the absorption of heat. In practice, the carbon (coke) is heated to redness, and steam is blown through it. The absorption of heat causes the temperature of the coke to fall and the reaction soon ceases. A continuous supply of heat is provided by blowing alternate blasts of steam and air through the mass of coke. The air starts combustion again and reheats the coke, if its temperature has not fallen too low. This reaction may be therefore carried out at temperatures where it occurs with satisfactory velocity without the aid of a catalyst.

Review Exercises

- 1 Why do some chemical changes appear to stop long before the quantities of substances added in the beginning are consumed?
- 2 When can a reversible reaction be said to have attained equilibrium?
- 3 Would the search for a catalyst which would accelerate the decomposition of water into hydrogen and oxygen at 20° be worth while? Explain.

- 4 Why does the reaction of hydrogen and oxygen at temperatures below 1000° appear to be irreversible? What evidence is there that this reaction is reversible? What conclusion might be reached if this reaction could be observed at the temperature of the sun?
- 5 The compound called zeolite, $\text{NaH}_2\text{AlSiO}_7$, is used to soften water. When hard water flows through a layer of this material, the sodium is replaced by calcium and $\text{Ca}(\text{H}_2\text{AlSiO}_7)_2$ is formed, the sodium ion remaining in solution. To restore the zeolite to its former condition, so that it may be used again, the calcium compound is heated with a solution of NaCl . What principle is involved here? Explain the action of NaCl .
- 6 The equilibrium constant for the reaction, $\text{N}_2 + \text{O}_2 \rightleftharpoons 2 \text{NO}$, at a given temperature is 0.0035. Explain this statement. What use might be made of information of this kind?
- 7 Describe and explain the effect of (1) increased pressure, (2) decreased temperature, (3) increased concentration of chlorine, and (4) decreased concentration of chlorine, upon the following reversible reaction: $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2 - 39,500 \text{ calories}$ (All the substances involved are gases.)
- 8 $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$. Compare the speeds of the forward and reverse reactions (1) when A and B are first mixed, (2) at equilibrium, (3) at time intervals between (1) and (2). How do the concentrations of A, B, C, and D change from the time the mixture of A and B is first made until equilibrium is reached?
- 9 What effect does an increase in pressure have upon the equilibrium condition of each of the following reactions?



- 10 The equilibrium mixture which results, under a total pressure of 1 atm, when sulfur dioxide and oxygen are brought together, contains 50 per cent by volume of SO_2 , $16\frac{2}{3}$ per cent of O_2 , and $33\frac{1}{3}$ per cent of SO_3 . Calculate the equilibrium constant.
- 11 State in words the meaning of the equilibrium constant (0.0035) in question 6.
- 12 How is the speed of a reaction determined?

Name the different factors that influence the speed of a reaction

- 13 Connect the following statement Equilibrium is the condition which is reached when a reversible reaction has proceeded as far as it can be made to go in one direction
- 14 Connect the following statement When a reaction has reached equilibrium no further reaction takes place
- 15 The conversion of a mixture of nitrogen and hydrogen into ammonia (page 430) is very slow at 400° . Why is it not practical to carry out this reaction at 1000° , at which the speed of the reaction would be much faster?
- 16 What factors that influence the speed of a reaction may be changed without affecting the equilibrium constant of the reaction?
- 17 State Le Chatelier's principle. Apply it to the effect of an increase in pressure upon a reversible reaction involving gases, to the effect of an increase in the concentration of one of the reacting substances; and to the effect of the addition of heat to a reaction in which heat is evolved by the forward reaction.
- 18 What is the distinction between the quantity of a substance and the concentration of the same substance? Explain, by using suitable illustrations, the conditions under which each of these terms can be used correctly.
- 19 According to the general rule concerning the effect of temperature upon the speed of a reaction, how many grams of a substance can be produced per minute at 100° if 1 g of the substance is produced in one minute at 0° ?

Assume concentrations and other conditions are the same for the two temperatures

- 20 When the reaction, $A + B \rightleftharpoons C$, has reached equilibrium, it is found that the concentrations of A, B, and C are, respectively, 2, 3, and 1 gram-molecular weights per liter. Calculate the equilibrium constant of the reaction.
- 21 What were the original concentrations of A and B, at constant volume, in the reaction of the preceding exercise if there was zero concentration of C at the beginning of the reaction?
- 22 Calculate the equilibrium constant for the reaction, $A + B \rightleftharpoons 2C$, if the concentrations of A, B, and C at equilibrium are, respectively, 3, 3, and 2 gram-molecular weights per liter.

References for Further Reading

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- Hogness, T. R., and W. C. Johnson, *Qualitative Analysis and Chemical Equilibrium*. New York: Henry Holt and Company, 1937.
- Howe, H. E., *Chemistry in Industry*, vol. II, chap. I. New York: The Chemical Foundation, 1924-25 (2 vols.)
- J. Chem. Ed.*, 2, 631 (1925), 7, 2887 (1930), 9, 261, 2026 (1932), 11, 328 (1934)
- Treadwell, F. P., and W. T. Hall, *Analytical Chemistry*, vol. I, Part I. 9th ed., New York: John Wiley and Sons, 1937.

EQUILIBRIA INVOLVING IONS

The next step was also quite clear, the active molecules, which are active in regard to electricity (good electrolytes), are also active in regard to chemical properties, and that was the great step. I got that idea on the night of the 17th of May in the year 1883

ARRHENIUS

1. Introduction

We are concerned primarily, in this chapter, with states of equilibrium that exist in solutions and that involve different ions and also, in many instances, molecules. Temperature and pressure have little effect upon the equilibrium conditions of ionic reactions. Changes in the concentration of one ion, however, may have profound effects upon the concentrations of other ions involved in the same equilibrium. In this chapter, we shall be concerned, therefore, with several different types of ionic equilibria, particularly as these may be influenced by the addition or removal of one or more ions. We shall first study equilibria involving the ions and molecules of acids and bases. Accordingly, our first task is to define these terms more fully than we have done previously and to determine, as far as we can, the nature of their ionic behavior in solutions and in reactions in which they participate.

ACIDS AND BASES

In discussing acids in previous sections of this book, we have shown that they possess certain properties in common. With hydroxide-bases they form salts, they produce certain color changes in indicators; many of them react with the more active metals to liberate hydrogen, and many of them react

with salts by double decomposition, particularly if the acid thus liberated is a gas or if it decomposes to form a gaseous product. As regards composition, all acids contain hydrogen, but all compounds which contain hydrogen are not acids.

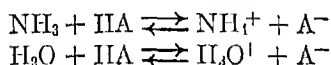
Acids and Bases Defined in Terms of Arrhenius's Theory

According to the theory of ionization proposed by Arrhenius, an acid is defined as a substance that releases at least a portion of the hydrogen that it contains as hydrogen ions when it is dissolved in water or certain other solvents. By this definition, the solution of any acid contains a certain number of free hydrogen ions per unit of volume, the exact number depending (1) upon the number of molecules of acid dissolved in a definite volume of solution, and (2) upon the tendency of these molecules to ionize as measured by the apparent degree of ionization of the acid. Bases are defined, in accordance with the same theory, as substances that produce hydroxyl ions in aqueous solutions.

2. A Newer Concept of Acids

The concept of an acid as a substance that must first liberate hydrogen ions spontaneously before it can act as an acid is no longer regarded as a satisfactory definition. Hydrogen ions are protons, and there is

little reason to believe that free protons can exist in solution to any greater extent than free electrons. Instead, it is thought that they either remain as parts of the molecules of the acid, or they leave these molecules to form covalent combinations with molecules or ions of other substances. An acid, therefore, forms ions in a solution only if its protons form combinations with molecules of the solvent (page 155). Thus, ammonium ion is produced in a solution of the acid HIA in liquid ammonia, and the hydronium ion is produced in a solution of the same acid in water:

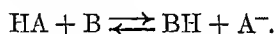


An acid is defined, therefore, as a proton donor, a substance that gives up protons to another substance. In so doing, the acid may produce ions as shown in the equations above, but this is not true of acids in general. For example, the hydronium ion, H_3O^+ , is an acid and, as such, it may react with A^- in the reverse reaction described in the equation above to form water and the acid HIA , in this instance, the acid is an ion itself, and it reacts to form neutral molecules. The distinguishing characteristic of an acid, therefore, is not its production of any one kind of ion, or its production of any ions at all, but its behavior as a source of protons that can be supplied for combination with the molecules or ions of other substances. Viewed in this light, dry hydrogen chloride is as much an acid as its aqueous solution. In fact, in aqueous solution molecules of hydrogen chloride probably exist only in small numbers, practically all of them having reacted with molecules of water to form hydronium (H_3O^+) ions. In this case the hydronium ion instead of the HCl molecule acts as the acid. The same is true of solutions of other strong acids such as HNO_3 , HBr , and HClO_4 . Since the real acid in solutions of all of these is the hydronium ion, it is easy to understand why these acids appear equally strong in aqueous solution.

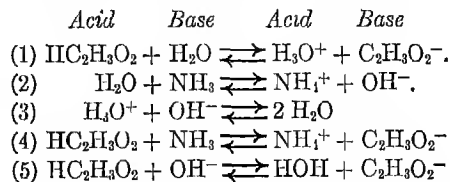
They do not appear to be equally strong acids in other solvents, such as benzene, in which ions corresponding to the hydronium ion cannot be formed, and in which molecules of the different acids, themselves, must act as the proton donors.

3 Bases and Their Reactions with Acids

In keeping with the new definition of an acid, a base is a substance that accepts protons from an acid. The following general equation serves to illustrate the roles played by both bases and acids:



B is the base and HA is the acid. One or both may be electrically charged or they may be uncharged molecules. The hydrogen ion (H^+) probably never exists free, it either remains in the acid molecule HIA or it combines, when A^- is formed, with another substance which acts as a base. The following equations illustrate reactions between acids and bases. In (1), for example, HA is $\text{HC}_2\text{H}_3\text{O}_2$, and B is the water molecule. In the reverse reaction, (H_3O^+) is the acid and the $\text{C}_2\text{H}_3\text{O}_2^-$ ion is the base. We see, here, illustrations of an electrically charged acid, H_3O^+ , and a neutral acid, $\text{HC}_2\text{H}_3\text{O}_2$. Likewise the base $\text{C}_2\text{H}_3\text{O}_2^-$ is charged, while H_2O is neutral. The reactions of other acids and bases are shown by the other equations:



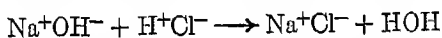
It will be noted that water, itself, acts as a base in accepting protons from acetic acid to form hydronium ions. Ammonia, the hydroxyl ion, and the acetate ion are also bases. In the forward reaction of (2) the water molecule reacts, however, as an acid in yielding a proton to the molecule of ammonia.

The views of acids and bases that we have

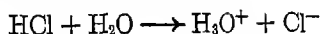
just discussed were first expressed comprehensively in theories formulated by Bronsted and Lowry. They are frequently referred to in chemical literature as the Bronsted concept of acids and bases. In keeping with this concept, a substance that can act either as an acid or as a base is described as *amphiprotic*.

4. Neutralization in Aqueous Solutions

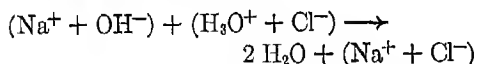
According to Arrhenius's theory, the neutralization of an acid and a base in aqueous solution is a reaction in which hydrogen ions of the acid and the hydroxyl ions of the base combine to form water, leaving the positive ions of the base and the negative ions of the acid to form a salt, e.g., NaCl



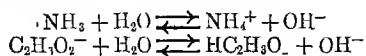
According to the point of view of Bronsted, the acid, when it is dissolved in water, reacts with water molecules



The sodium hydroxide—an ionic compound—is completely ionized. When solutions of the two substances are mixed, the following reaction occurs



Actually, according to the Bronsted concept, sodium hydroxide is a salt. When dissolved in water, the anion, OH^- , of this salt acts as a base when a substance that can supply protons is added to the solution. In aqueous solutions, other bases also produce hydroxyl ions by reacting with molecules of water. For example,



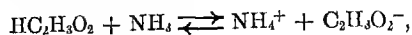
In aqueous solutions, therefore, the base that reacts with an acid is the hydroxyl ion.

The tendency of this base (OH^-) to remove protons from acids is stronger than that of other bases, such as NH_3 and $\text{C}_2\text{H}_3\text{O}_2^-$, because water, which is produced

by OH^- ion when it acts as a base, is much less ionized (is a weaker acid) than the substances produced when other bases accept protons from acids.

5. Protolysis

According to the Bronsted concept, neutralization is a special case of a reaction between an acid and a base in which *molecules of water are produced*. In several of the reactions listed on page 435, the reaction of an acid with a base, e.g.,



does not produce water. The fundamental characteristic of these reactions is the *transfer of protons* from acid to base. A reaction in which this transfer occurs is called a *protolytic reaction*.

6. Present Status of the Concepts of Acids and Bases

It is unfortunate for the student that acids and bases are still defined and treated in chemical literature from both the old and the new points of view. The new concepts are favored, in general, because they can be applied to solutions in solvents other than water, and even to acids and bases that are not dissolved at all. The older concepts are still in evidence largely because most of the reactions between acids and bases that are studied or used in the laboratory occur in aqueous solutions, for which our choice of definitions is not a matter of great moment.

For our present study, we shall make considerable use of the older concepts, since the solutions with which we are concerned are those in which water is the solvent, and since, also, we shall deal with many weak electrolytes, most of which are acids. After all, there is no fundamental difference between the two definitions of acids, both include the principle that an acid must yield hydrogen ions to another substance. In aqueous solutions, according to the older theory, hydrogen ions are liberated by the acid and are then free to act with a base, the later theory also deals with hydrogen ions and, in aqueous solution, these are hydrated. When these hydrated hydrogen ions react with a base, however, it is the hydrogen ion or proton that reacts, and the water

molecule of the hydrated ion is set free again. Thus, the essential point of difference involves the method by which ions are liberated from the acid, and also, of course, there is the question of whether or not the acid must first ionize before it can react. The later theory assumes that in solvents unlike water and like benzene there is no preliminary ionization of the acid, molecules of the acid react directly by transferring protons to the base.

7 Strengths of Acids, Bases, and Salts

Since early in the history of the Arrhenius theory, the strengths of electrolytes have been compared by determining their apparent degrees, or percentages, of ionization in

aqueous solutions of the same concentration. These comparisons have been based, for the most part, upon apparent degrees of ionization as measured by the conductivity method (page 477). The values thus obtained are fairly accurate measures of strength—for aqueous solutions at least—regardless of which theory of electrolytes we accept. Certain strong electrolytes may be completely ionized, but even for these compounds the apparent degree of ionization is a measure of the extent to which their ions are independent and are not restricted by attractions that exist between them and other ions or molecules in the solution. To

TABLE 23

The Strengths of Common Electrolytes¹ as Measured by Their Degrees of Ionization in Aqueous Solutions

Acid		Percentage ionized	
Hydrochloric,	HCl	N/10	92
Nitric,	HNO ₃	N/10	92
Sulfuric,	H ₂ SO ₄	N/10 (H ⁺ , HSO ₄ ⁻)	90
	H ₂ SO ₄	N/10 (HSO ₄ ⁻ → H ⁺ + SO ₄ ⁼)	60
Oxalic,	H ₂ C ₂ O ₄	N/10 (H ⁺ , HC ₂ O ₄ ⁻)	40
	H ₂ C ₂ O ₄	N/10 (HC ₂ O ₄ ⁻ → H ⁺ + C ₂ O ₄ ⁼)	1
Carbonic,	H ₂ CO ₃	M/10 (H ⁺ , HCO ₃ ⁻)	0.17
Hydrosulfuric,	H ₂ S	M/10 (H ⁺ , HS ⁻)	0.07
	H ₂ S	M/10 (HS ⁻ → H ⁺ + S ⁼)	0.0001
Phosphoric,	H ₃ PO ₄	M/10 (H ⁺ , H ₂ PO ₄ ⁻)	27
	H ₃ PO ₄	M/10 (H ₂ PO ₄ ⁻ → H ⁺ + HPO ₄ ⁼)	0.1
	H ₃ PO ₄	M/10 (HPO ₄ ⁼ → H ⁺ + PO ₄ ⁼)	0.0001
Acetic,	HC ₂ H ₃ O ₂	N/10	1.34
Hydrocyanic,	HCN	N/10	0.01
Bases			
Potassium hydroxide,	KOH	N/10	91
Sodium hydroxide,	NaOH	N/10	91
Barium hydroxide,	Ba(OH) ₂	N/10	77
Ammonium hydroxide,	NH ₄ OH	N/10 (NH ₃ + HOH ⇌ NH ₄ ⁺ + OH ⁻)	1.3
Salts			
Potassium chloride,	KCl	N/10, and all salts of the type M ⁺ X ⁻ ,	86
Calcium chloride,	CaCl ₂	N/10, and salts of the type M ⁺⁺ X ₂ ⁻ ,	75
Cupric sulfate,	CuSO ₄	N/10, and salts of the type M ⁺⁺ X ⁼ ,	39
Mercuric chloride,	HgCl ₂	N/10, one of the few exceptions,	1

¹ The degree of ionization of a given substance varies with the temperature. Most of the values in this table were determined at 18° C. In the portion of the table dealing with salts M represents a metal and X a non-metal or a negative radical, the valences are indicated by the + or - signs.

the extent that the ions are thus restricted — for example, by the attraction between a positive ion and negative ions in the same solution — their mobility is decreased, and the ions can contribute only in a limited manner to the strength of the electrolyte if, as we believe, the behavior upon which strength depends involves the ions of the substance.

The strengths of certain electrolytes, as measured by the method just described, are shown in Table 23. For the acids of this table, the symbol H^+ has been used in place of $H^+ \cdot H_2O$ or H_3O^+ for the hydrated hydrogen ion.

8. Strengths of Acids and Bases in Terms of the Bronsted Theory

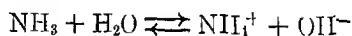
In terms of Bronsted's theory of acids and bases, the relative strength of an acid depends upon its tendency, as compared with other acids, to give up protons for reaction with a basic substance. The strength of a base depends upon the tendency of the base to combine with protons, that is, its attraction for the protons that an acid can supply. Experimentally, evidence concerning the relative strengths of acids and bases in aqueous solutions can be secured by measuring the apparent degrees of ionization of the solutes. For acids, the production of ions depends upon (1) the tendency of the acid to yield protons, and (2) the tendency of water to combine with protons to form H_3O^+ ions. Of these two factors, (1) varies for different acids but (2) is the same for all. The difference in the number of ions produced by equal molecular concentrations of different acids depends essentially, therefore, upon factor (1), and hence, we may look upon the apparent degree of ionization of the acid as a measure of its strength, regardless of the particular concept of acids that we wish to adopt.

9. A Comparison of the Strengths of Acids and Bases

Hydrochloric acid is classified as a strong acid, because 92 per cent of its molecules in a 0.1 N solution — containing one tenth of a gram-molecular weight of HCl per liter — appear to be ionized. Acetic acid in a solution of the same concentration appears to

be ionized only to the extent of 1.3 per cent of its molecules. It is evident, therefore, that one liter of the solution of hydrochloric acid contains many more hydrogen (or hydronium) ions than one liter of a solution of acetic acid. Acetic acid is classified, therefore, as a weak acid.

Sodium hydroxide is classified as a much stronger base than ammonium hydroxide, the apparent ionization of sodium hydroxide in a 0.1 N solution is 91 per cent, and that of ammonium hydroxide is only 1.3 per cent. The former is a strong base, because all of its hydroxyl ions are free to act as a base by accepting protons, although they act, because of interionic attraction, as if only 91 per cent of them were free at any one time. The small number of ions in the solution of ammonium hydroxide indicates that ammonia and water do not react to produce many ions.



Hence, in this solution there are few hydroxyl ions, at any one time, to act as a base, furthermore, ammonia itself cannot have a very strong capacity for combining with protons (as compared with the hydroxyl ion), because if it did, it would remove more of them from molecules of water and would thus produce more ions, when it is dissolved in water, than it actually does.

10. Strengths of Acids and Bases as Measured by Indicators

The strengths of different acids and bases can be compared, also, by means of appropriate indicators. The color that an indicator imparts to an aqueous solution in which it is dissolved depends upon the form in which the indicator exists in the solution, and the form depends, in turn, upon the concentrations of hydrogen and hydroxyl ions. If solutions containing the same molecular concentrations of hydrochloric and acetic acids are treated with equal quantities of the indicator *methyl violet*, the colors of the two solutions will not be the same. For N/10

hydrochloric acid solution the color is bluish-green, and for N/10 acetic acid it is violet. If the N/10 solution of hydrochloric acid is sufficiently diluted, it gives the same color with methyl violet as the N/10 solution of acetic acid. Blue litmus turns red in N/10 hydrochloric acid and acetic acid solutions, but it is not noticeably affected by a solution of hydrogen sulfide, H_2S , of approximately the same concentration. Since differences in the color of an indicator are the result of reactions involving hydrogen ions and the indicator, hydrochloric acid evidently makes available for reaction with the indicator more hydrogen ions than an equal number of molecules of acetic acid, and acetic acid more than hydrogen sulfide.

11. The Ionization of Salts

A salt can be defined as a compound composed of the cations (+) of a metal, or of positively charged radicals, such as NH_4^+ , and the anions (-) produced when certain acids, such as HCl or H_2SO_4 , transfer protons to a base. This definition must be carefully worded. It is necessary to specify "certain acids," because some acids, such as HOH or H_3O^+ , do not form anions that can be regarded as the anions of salts, and some acids do not, of course, form any ions at all when they give up protons to a base.

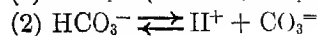
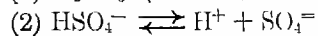
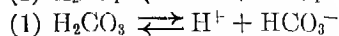
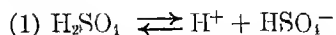
All true salts by this definition are ionic compounds and, therefore, are strong electrolytes, then apparent degrees of ionization are relatively high (Table 23). A few pseudo-salts, such as mercuric chloride, are ionized only to about the same extent as acetic acid and ammonium hydroxide, but such compounds are rare.

From our knowledge of their ionic character we should expect salts to be ionized completely in aqueous solutions, and unquestionably they are, as we have already pointed out on page 242 and again on page 413. The apparent contradiction of this statement by data on the degree of ionization as measured by the conductivity method has been explained in terms of the Debye-

Huckel theory by the decrease in conductivity resulting from interionic attraction in even moderately dilute solutions of the salts. If the interionic attraction theory is valid — and there is every reason to believe that it is — salts composed of divalent or trivalent ions should have smaller apparent degrees of ionization than salts composed of univalent ions. An ion that carries two units of positive charge should attract chloride ions, for example, more strongly, should produce greater resistance to the movement of these ions through the solution, and should, therefore, have a greater effect in reducing the electrical conductivity than a positive ion possessing only one unit of charge. How well the facts support this proposition may be observed by an inspection of the degrees of ionization of different salts (page 437). Salts consisting of univalent ions, such as NaCl , NaNO_3 , and KCl , in N/10 solutions are ionized to an extent of 80 to 90 per cent. Salts containing one divalent and one univalent ion are ionized to an extent which is about 10 per cent less, on the whole, than the first group. Salts containing two divalent ions show an apparent degree of ionization of approximately 40 per cent.

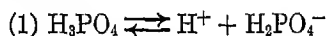
12 The Ionization of Dibasic and Tribasic Acids, Acid Salts

Since a molecule of a dibasic acid contains two hydrogen atoms which may be liberated as protons for reactions with a base, we may think of such an acid as ionizing in two steps. The steps in the ionization of sulfonic and carbonic acids are shown below as equations in which we have omitted the part played by water in producing the ions. In (1) the acid ions, *bisulfate* and *bicarbonate*, are produced. In (2) normal anions of the acids are liberated, that is, sulfate and carbonate ions.



In moderately concentrated and in concentrated solutions of sulfuric acid, experimental evidence indicates that reaction (1) provides most of the ions, whereas reaction (2) forms very few sulfate ions. In very dilute solution, reaction (2) occurs to a greater extent. If a base is added to remove the hydrogen ions, reaction (2) runs to completion, and the solution contains, at the end of the reaction, sulfate rather than bisulfate ions. If the acid and sodium hydroxide are mixed in approximately equal molecular concentrations, the solution, after the reaction, contains sodium and bisulfate ions. If this solution is evaporated sodium bisulfate crystallizes.

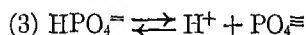
A tribasic acid ionizes in three stages. A moderately concentrated solution of phosphoric acid (H_3PO_4), for example, contains chiefly hydrogen ions and dihydrogen phosphate ions



In more dilute solutions, the following reaction occurs, forming the monohydrogen phosphate ion



In very dilute solution appreciable concentrations of the simple phosphate ion may be formed



The extent to which the monohydrogen phosphate ion, HPO_4^{2-} , ionizes is very slight in solutions of the usual concentrations.

Corresponding to the three phosphate ions that phosphoric acid forms, there are three sodium salts: sodium dihydrogen phosphate (NaH_2PO_4), sodium monohydrogen phosphate (Na_2HPO_4), and sodium phosphate (Na_3PO_4). The first two are *acid* salts, the last is the *normal* phosphate.

An *acid salt* may be defined as a salt that contains an anion that can act as an acid, the solution of an acid salt contains the ions of the acid as well as those of the normal salt. Thus, a solution of potassium bisulfate,

KHSO_4 , contains potassium, hydrogen, and sulfate ions. In addition to these, the acid salt also gives the acid-salt anion, HSO_4^- .

The apparent degrees of ionization of a few dibasic and tribasic acids are given, for each stage of the ionization of the molecule, in Table 23 (page 437). Attention is called to the great difference in the extents to which the first stage and the second or third stages of the ionization of these acids take place.

The terms *monoprotic*, *diprotic* and *triprotic* are sometimes used in referring to acids that contain, per molecule, one, two, and three hydrogen atoms, respectively, that can be liberated as protons for reactions with bases.

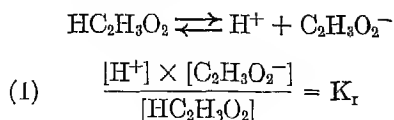
13 Diacid and Triacid Bases, Basic Salts

For each sodium ion in sodium hydroxide there is one hydroxyl ion, the formula is Na^+OH^- . The weight (grams) corresponding to this formula requires for its complete neutralization one gram-molecular weight of a monobasic acid — one gram-ion weight, or 1.008 g, of H^+ . Sodium hydroxide, therefore, is a *monoacid base*. Barium hydroxide, $\text{Ba}(\text{OH})_2$, and calcium hydroxide, $\text{Ca}(\text{OH})_2$, are *diacid bases*, and aluminum hydroxide, $\text{Al}(\text{OH})_3$, and ferric hydroxide, $\text{Fe}(\text{OH})_3$, can be classified as *triacid bases*. *Basic salts* sometimes result from the partial neutralization of diacid and triacid bases. Basic cupric chloride, $\text{Cu}(\text{OH})\text{Cl}$, and basic bismuth nitrate, $\text{Bi}(\text{OH})_2\text{NO}_3$, are examples of such salts. They may react with additional acid to form normal salts, such as CuCl_2 and $\text{Bi}(\text{NO}_3)_3$.

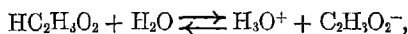
14 Ionization Constants

Since the reactions by which ions are produced from molecules are reversible, we may set up equilibrium equations for these reactions and, knowing the apparent concentrations of the ions and molecules involved in these equilibria, we can determine the equilibrium constants for the reactions. As applied to reactions of this kind these constants are called *ionization constants*.

For the ionization of acetic acid, the equilibrium equation is



If we take into account the formation of hydrated hydrogen, or hydronium, ions in an aqueous solution, the equation for the ionization of the acid is



and the ionization constant is defined as

$$(2) \quad K_i' = \frac{[\text{H}_3\text{O}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2] \times [\text{H}_2\text{O}]}$$

Of the four concentrations represented in this equation, the concentration of water, $[\text{H}_2\text{O}]$, is constant or may be so regarded for all dilute solutions. The concentration of water is $1000 \text{ g} - 18 \text{ g} = 982 \text{ g}$ gram-molecular weights or moles per liter, this concentration is so much greater than the concentration of any other substance in the solution, that it would not be changed greatly even if all of the H_3O^+ and $\text{C}_2\text{H}_3\text{O}_2^-$ ions were changed into molecules of acetic acid and water. Hence we may write the equation as

$$(3) \quad \frac{[\text{H}_3\text{O}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K_i' \times [\text{H}_2\text{O}] = K$$

Since $[\text{H}_3\text{O}^+]$ in equation (1) and $[\text{H}^+]$ in equation (3) represent the same thing and have the same value, the ionization constant, K , of equation (3) is identical with the constant of equation (1).

15 Calculation of the Ionization Constant of Acetic Acid

To determine the numerical value of the ionization constant of acetic acid, we must know the concentrations at equilibrium of hydrogen ions, acetate ions, and undissociated acetic acid molecules. These can be found from the percentage of ionization of the acid. In N/10 acetic acid solution, 1.33 per cent of the molecules are ionized at 18°C . Now the N/10 solution contains 0.1 of a gram-molecular weight of the acid per liter. In calculating ionization constants, all concentrations are expressed in terms of molar

quantities, e.g., 0.1 gram-molecule of acid per liter. Of this quantity of acetic acid, 1.33 per cent or $0.1 \times 0.0133 = 0.00133$ gram-molecular weight produces ions. Since each molecule in ionizing produces one hydrogen and one acetate ion, the molar (or ionic) concentration of each ion in this solution will be 0.00133 gram-ion per liter. The concentration of the acetic acid *that is not ionized* is the quantity added (per liter) minus the quantity that ionizes, or $0.1 - 0.00133 = 0.09867$ gram-molecular weight per liter. These values can now be substituted in the equilibrium equation, thus permitting us to calculate K_i .

$$\frac{0.00133 \times 0.00133}{0.09867} = K_i =$$

$$\frac{0.00000169}{0.0987} = 0.000018$$

The value 0.000018 may also be written as 1.8×10^{-5} .

16 The Effect of Dilution upon the Ionization Constant

Let us now dilute the 0.1 normal solution of acetic acid to ten times its volume. The concentration of the acid is now 0.01 normal, and one liter contains only one tenth as much of the solute as one liter of the 0.1 normal solution contains. If the degree of ionization of the acetic acid were the same in the two solutions, the value of K_i for the ionization in the second solution would be smaller than for the first. The value of each concentration would be decreased to one tenth of its original value and the equilibrium constant would be

$$\frac{0.00013 \times 0.00013}{0.009869} = \frac{0.0000000169}{0.009869} =$$

$$1.8 \times 10^{-6}$$

We have learned, however, that the apparent degree of ionization increases with the dilution (page 411). Hence, in the more dilute solution, the ionic concentrations will be larger than those indicated above, and the

concentration of the undissociated acid will be smaller. The changes in concentration upon dilution are found to be exactly those required to restore the original value of K_i . This can be proved as follows. The apparent degree of ionization of acetic acid in a 0.01 normal solution (at 18° C) is 4.17 per cent. For this solution, therefore, the concentration of the non-ionized acid is 0.01 - (0.0417×0.01) , or 0.009583, gram-molecular weight per liter. Each ionic concentration is 0.01×0.0417 , or 0.000417, gram-ion per liter. Substituting these values in the equilibrium equation, we find that the value of K_i again proves to be 1.8×10^{-5} .

$$\frac{0.000417 \times 0.000417}{0.009583} = 0.000018$$

The same value of K_i holds fairly well for other concentrations of the acid, so long as the solutions are at least only moderately concentrated, and its constant value over a considerable range of concentrations has great significance. If the equilibrium constant of a reaction has any real meaning, it must be constant, that is, it must have the same value at the same temperature for different concentrations of the substances involved. Since the ionization constant for acetic acid is really constant, the principles of equilibrium, and the law of mass action, or molecular concentration, upon which these principles of equilibrium depend, can be applied at least to a dilute solution of this acid, and for like reasons to the solutions of other weak electrolytes. Reasons why K_i is not constant in concentrated solutions will be given in the following sections.

17. Ionic Equilibria of Strong Electrolytes

When we attempt to determine the ionization constants of strong electrolytes, such as NaOH or NaCl, we find that K_i for these substances has no definite value but varies greatly as the concentration changes. This variation of K_i means that for the solutions of these substances the law of molecular concentration and the principles governing

chemical equilibrium are not strictly applicable.

This behavior of strong electrolytes might be anticipated since we have excellent reasons to believe that these substances are probably completely ionized. We have already learned (page 414) that the apparent degree of ionization of a strong electrolyte differs for different concentrations, not because more electrolyte ionizes in dilute solutions, but because of variation in the ionic attraction as a concentrated solution is diluted. This variation leads to an observed conductivity which is less than would be predicted upon the basis of the number of ions actually present in a definite volume of the solution. The more concentrated the solution, the denser the ions in that solution become, and the more restricted is the mobility of an ion because of the forces exerted upon it by other ions. We should not expect to find constant values for the "equilibrium constant" of sodium chloride, or similar substances, for the simple reason that there is no equilibrium, and there is no equilibrium because there is no reversible reaction between ions and molecules.

18. Activity and Activity Coefficients

The failure of the law of mass action or molecular concentration is not confined to solutions of strong electrolytes. The law fails for all reacting systems consisting of particles of any kind, if these particles are crowded closely together. We have learned that molecules of gases exert an attraction for each other, and that for liquids this attraction is even greater. Furthermore, in solutions varying degrees of attraction exist between molecules or ions of different solutes and molecules of solvent. All of these influences retard the movement of the particles, regardless of whether they are molecules or ions, and consequently cause a decrease in the speed of the reaction between any two varieties of particles in the mixture. We cannot, therefore, expect the speed of reactions to be proportional to the molecular

or 3.35×10^{26} molecules. This number may be written as 33,500,000,000,000,000,000,000. The number of the molecules which produce ions is 60,500,000,000,000,000. This means that one molecule in approximately 552,000,000 ionizes at ordinary temperatures. This is about 0.0000002 per cent.

20 The Ionization Constant of Water

The ionization constant of water is given by the equation

$$\frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{HOH}]} = K_i$$

Because of the apparently slight degree of ionization of water, K_i must be very small. The numerical value of the constant may be calculated by substituting the values for the ionic concentrations and the concentration of the non-ionized water (as given above) in this equation. The portion of the water which does not ionize is almost equal to the total quantity and may be so regarded. Furthermore, when the equilibrium is disturbed and the reaction adjusts itself to restore equilibrium, the quantity of undissociated water that is formed or that disappears is so slight that *the total concentration of water may be regarded as constant*. Now the molecular concentration of non-ionized water is 55.5 gram-molecular weights per liter, the concentration of each ion (at ordinary temperatures) is 0.0000001 gram-ion per liter. The dissociation constant, therefore, is

$$\frac{0.0000001 \times 0.0000001}{55.5 - 0.0000001} = \frac{1 \times 10^{-14}}{55.5} = 1.9 \times 10^{-16}$$

Since the concentration of non-ionized water is enormous as compared with the extremely small concentrations of the ions, and since it is also practically constant, it is more convenient to write the equation for the equilibrium constant of water as follows

$$[\text{H}^+] \times [\text{OH}^-] = K_i \times [55.5] = K_{\text{rw}}$$

The constant, K_{rw} , is equal, therefore, to the product of the gram-ion concentrations of the ions of water (H^+ and OH^-). At ordinary temperatures K_{rw} has the value 1×10^{-14} . At higher temperatures, K_{rw} has somewhat greater values.

21. Hydrogen and Hydroxyl Ion Concentrations of Solutions

If the product of their concentrations is 1×10^{-14} , the concentrations of hydrogen and hydroxyl ions are each 1×10^{-7} gram-ion per liter at ordinary temperatures. This is the concentration in *pure water*. In any *solution* containing the two ions, the product of their concentrations must also always be 1×10^{-14} . Pure water, which contains equal concentrations of the two ions, represents a condition of exact neutrality. Likewise, any solution is exactly neutral if it contains 1×10^{-7} gram-ion each of hydrogen and hydroxyl ions. This does not mean that *any* solution that contains the two ions must contain the same concentration of each. If an acid is added to water, the concentration of the hydrogen ion is increased, if a base is added the concentration of the hydroxyl ion is increased. We must understand, however, that both kinds of ions are present in every aqueous solution, even if the solute produces neither ion, water itself produces both. As the concentration of the hydrogen ion increases, the concentration of the hydroxyl ion must decrease, and vice versa. The product of the two concentrations (temperature remaining constant) must always be the same as it is in pure water, 1×10^{-14} .

Let us consider the ionic concentrations in a N/10 solution of hydrochloric acid. If we may assume that this is completely ionized, the concentration of the hydrogen ion in this solution is 0.1 gram-ion per liter. The concentration of the hydroxyl ion is found by solving for $[\text{OH}^-]$ in the equation

$$\begin{aligned} 0.1 \times [\text{OH}^-] &= 1 \times 10^{-14} \\ [\text{OH}^-] &= \frac{1 \times 10^{-14}}{1 \times 10^{-1}} = 1 \times 10^{-13} \end{aligned}$$

The concentration of H^+ in N/1000 HCl solution is 0.001, if the acid is completely ionized. This may be written as 1×10^{-3} . Hence, $[OH^-]$ is 1×10^{-11} .

$$1 \times 10^{-3} \times [OH^-] = 1 \times 10^{-14}$$

$$[OH^-] = 1 \times 10^{-11}$$

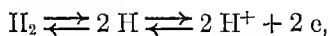
A solution of N/1000 sodium hydroxide solution, if completely ionized, contains 0.0001 gram-ion of OH^- per liter. This solution, therefore, contains 1×10^{-10} gram-ion of H^+ per liter.

$$[H^+] \times 1 \times 10^{-4} = 1 \times 10^{-14}$$

$$[H^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10}$$

22 The Hydrogen Electrode, Comparisons of Hydrogen Ion Concentration

A direct method of determining the hydrogen ion¹ concentration of a solution depends upon the determination of the electromotive force, or potential, between free hydrogen and the hydrogen ions in that solution. An electrode consisting of a gold or platinum wire or foil and covered with finely divided platinum is placed in the solution, and pure hydrogen is passed over it. The hydrogen is adsorbed by the platinum, which catalyzes the dissociation of hydrogen molecules into hydrogen atoms. The atoms of hydrogen then establish equilibrium with the hydrogen ions of the solution. The complete reaction is represented by the following equation:



where e represents an electron. When the concentration of the hydrogen ion is decreased, the equilibrium is disturbed, and the reaction proceeds toward the right. As hydrogen atoms change into ions, electrons are left on the electrode and increase its negative charge. On the other hand, an increase in the concentration of the hydrogen ion causes the reaction to go to the left, and ions are converted into neutral atoms and

¹ As elsewhere, we are using here the hydrogen ion, H^+ , instead of the hydronium, H_3O^+ , to represent the positively charged ion of an acid in aqueous solutions.

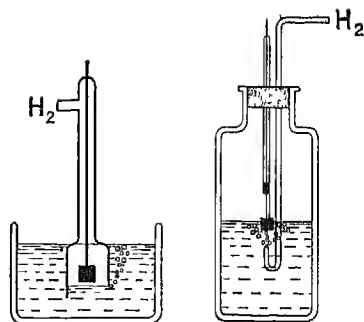


Figure 200 Hydrogen Electrodes

molecules. This change removed electrons from the electrode and decreases its negative charge. If the hydrogen electrode is placed in a circuit with another electrode whose charge remains constant, changes in the potential may be regarded as changes in the electrical charge of the hydrogen electrode resulting from changes in hydrogen ion concentration. Comparisons of the hydrogen ion concentrations of different solutions can thus be made.

23 pH or the Hydrogen Ion Index

Instead of expressing the concentration of hydrogen ions in gram-ions per liter, the concentration is often expressed in terms of pH, or the hydrogen ion index. The term pH is an abbreviation of the expression "potential of hydrogen."

Numerically, the pH of a solution is the logarithm of the number of liters of the solution that contains one gram-atomic weight (1.008 g) of hydrogen as H^+ ion. The same statement may be expressed in the form of an equation:

$$pH = \log \frac{1}{[H^+]},$$

where $1/[H^+]$ is, of course, the reciprocal of the concentration of H^+ per liter, and is equal to the number of liters containing one gram-ion weight of hydrogen ion.

24 The pH of Water and of Solutions

Pure water contains 0.0000001 gram-ion of H^+ per liter. Hence the pH of water is

$$pH = \log 1/0.0000001 = \log 10,000,000$$

Now the common logarithm of a number is the exponent of 10 which shows the power to which 10 must be raised to give the number. The logarithm of 10 is 1, of 100, 2, of 1000, 3, and 10,000,000, 7. The pH of pure water therefore is 7.

In a solution containing an acid the concentration of H^+ is greater than it is in water. This means that the number of liters in which one gram-ion of H^+ is contained is smaller for the solution of the acid than for water, consequently, *the pH is smaller the greater the concentration of H^+* . In an alkaline solution, the pH is greater than 7.

If we may assume that a 0.001 N solution of HCl is completely ionized, the concentration of the hydrogen ion is 0.001 N, and one gram-ion weight is contained in 1000 liters. The logarithm of 1000 is 3 ($1000 = 1 \times 10^3$) and 3, therefore, is the pH of this solution. The relationships between hydrogen ion concentration and pH, also the corresponding OH^- concentrations, are shown in Table 24.

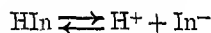
25. Use of Indicators in Measuring pH Values

The concentration of hydrogen ion, or the pH, of a solution can be measured by means of the hydrogen electrode (page 445) or by the use of other electrodes whose potentials are determined by the concentration of H^+ of the solutions in which they are im-

mersed. A simpler, but less quantitative method depends upon the colors produced when different indicators are added to the solutions. This method is used, ordinarily, when only approximate values of the pH are required. To explain the use of indicators for this purpose we must first understand why they change color as the concentration of hydrogen ion varies.

26. Theory of Indicators

An indicator that exhibits two colors possesses two different structural arrangements of its atoms. Of these two forms, one may be regarded as non-ionized, and the other, as a substance resulting from the ionization of the first form, most indicators are weak acids, and we shall so regard them in this discussion. Let us designate the non-ionized form of the indicator as HIn and the ionized form as In^- . In an aqueous solution the following equilibrium is established



If a base is added to this solution, the hydrogen ion is removed (to form molecules of water), and the reaction tends to run more completely to the right. The effect is to increase the concentration of In^- and to decrease the concentration of HIn . The color of the solution consequently becomes that of the ion, In^- , in an alkaline solution. When an acid is added, the concentration of the hydrogen ion is increased. This causes an increased speed of the reaction toward the left, and in restoring equilibrium, the concentration of In^-

TABLE 24

Relation Between Hydrogen Ion Concentration and pH (with Corresponding OH^- Concentrations)

Conc of H^+ (N)	No. of liters which must be taken to obtain 1 gram-ion of H^+	pH	Conc of OH^- (N)
1 N or 1×10^0 N	1 or 1×10^0	0	1×10^{-11}
0.1 N or 1×10^{-1} N	10 or 1×10^1	1	1×10^{-13}
0.01 N or 1×10^{-2} N	100 or 1×10^2	2	1×10^{-12}
0.001 N or 1×10^{-3} N	1,000 or 1×10^3	3	1×10^{-11}
0.0001 N or 1×10^{-4} N	10,000 or 1×10^4	4	1×10^{-10}
0.00001 N or 1×10^{-5} N	100,000 or 1×10^5	5	1×10^{-9}
0.000001 N or 1×10^{-6} N	1,000,000 or 1×10^6	6	1×10^{-8}
0.0000001 N or 1×10^{-7} N	10,000,000 or 1×10^7	7	1×10^{-7}
0.00000001 N or 1×10^{-8} N	100,000,000 or 1×10^8	8	1×10^{-6}
0.000000001 N or 1×10^{-9} N	1,000,000,000 or 1×10^9	9	1×10^{-5}
0.0000000000001 N or 1×10^{-13} N	10,000,000,000,000 or 1×10^{13}	13	1×10^{-1}

is decreased and that of HIn is increased. In an acid solution, therefore, the color is that which is characteristic of the non-ionized form of the indicator HIn . The change from one color to the other might be expected to occur in an exactly neutral solution ($\text{pH} = 7$). This, however, is not the case. Each indicator changes within a certain range of pH , and this is usually not a pH of 7. The differences in the pH values required to change the colors of different indicators depend upon several factors. The number of In^- and H^+ ions which a given number of

molecules of the indicator is able to produce is, perhaps, one of the most important of these factors. The greater the tendency of the indicator to ionize, of course, the more H^+ ions are required to reverse the reaction and reduce $[\text{In}^-]$ to a sufficiently low value so that its color will not predominate. The relative intensity of the colors of the two substances is also an important factor.

27 Examples of the Use of Indicators in Comparing Hydrogen Ion Concentrations

The colors of solutions of some of the

TABLE 25

Indicator Colors in Solutions of Different pH

R, red, B, blue, Y, yellow, V, violet, P, purple, O, orange, C, colorless, G, green, Ch, changing

Methyl violet	Methyl yellow	Methyl orange	Brom-phenol blue	Congo red	Sodium alizarin sulfonate	Methyl red	Brom-cresol purple	Brom-thymol blue	Litmus	Neutral red	Rosolic acid	Thymol blue	Phenolphthalein	Trimetabenzene	Indigo carmine	pH
Y	R	R	Y	B	Y	R	Y	Y	R	R	Y	R	C	C	B	0
G	R	R	Y	B	Y	R	Y	Y	R	R	Y	O	C	C	B	1
B	R	R	Y	B	Y	R	Y	Y	R	R	Y	Y	C	C	B	2
V	Ch	R	Y	V	Y	R	Y	Y	R	R	Y	Y	C	C	B	3
V	Y	O	G	V	Y	R	Y	Y	R	R	Y	Y	C	C	B	4
V	Y	Y	B	R	Y	Ch	Y	Y	R	R	Y	Y	C	C	B	5
V	Y	Y	B	R	Ch	Y	Ch	Y	R	R	Y	Y	C	C	B	6
V	Y	Y	B	R	V	Y	P	G	Ch	Ch	Ch	Y	C	C	B	7
V	Y	Y	B	R	V	Y	P	B	B	Y	R	Y	C	C	B	8
V	Y	Y	B	R	V	Y	P	B	B	Y	R	G	Ch	C	B	9
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	C	B	10
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	C	B	11
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	C	B	12
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	O	G	13
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	Y	O	Y	14

common indicators corresponding to different pH values are shown in Table 25. It should be understood that the change from one color to another usually does not occur at a definite pH but occurs, sometimes, through a considerable range of changing hydrogen ion concentrations.

The use of indicators in determining the pH of a solution is illustrated by the following examples. If a solution gives a yellow color when methyl red is added, we know that the pH of this solution is above 5 (Table 25). If the same solution gives a yellow color with moseley acid, we know that the pH is less than 7, but is between 5 and 7. If we find that the color of the solution is violet with sodium alizarin sulfonate and yellow with brom-cresol purple, the pH value is further restricted to a place between 5 and 6.

When the pH has thus been restricted to a small range we may proceed as follows. Let us say that we know that the pH lies between 8 and 10. Phenolphthalein changes from colorless to pink with increasing pH within this range. It becomes slightly pink at a pH of about 8.5, and the color increases in intensity up to about 9.6. If we make standard solutions containing known concentrations of hydrogen ions within this range and add the same number of drops of a solution of the indicator to each, a set of solutions will be obtained varying in intensity of color. If the solution of unknown pH is compared with these, after being treated with the same number of drops of the indicator solution, it will be found to match one of the standards, or perhaps to have a shade of color or an intensity which places it between two of the standards. For other ranges of pH, other indicators may be used in a similar manner.

28. The Importance of Hydrogen Ion Measurements and Control

The proper hydrogen ion concentration must be maintained to secure the results desired from many kinds of chemical change

in nature, in industry, and in scientific investigations. The pH of the blood of man must not vary far in either direction from an average value of 7.35. This pH indicates that the blood is slightly alkaline. The pH usually increases a little after a person eats, because the stomach draws upon the hydrogen ions of the blood to produce the hydrochloric acid needed for digestion. Measurements and control of hydrogen ion concentration are of importance in bleaching, dyeing, purification of water (pH affects the rate of filtration), corrosion of metals, manufacture of dyes and drugs, acidity of soils, sizing of paper, fermentations of sugar and starches, baking, and candy making. In analytical chemistry the separation and detection of several of the metallic ions depend upon the pH of the solutions containing the ions. Many other applications of pH measurements might be added, but those mentioned are indicative of their importance.

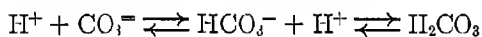
REACTIONS BETWEEN IONS

29. Will Ions A^+ and B^- Combine?

Many compounds are formed by reactions between ions in solutions. In all solutions containing two electrolytes, combinations of two pairs of ions are possible and may, or may not, occur. Let us consider two electrolytes, A^+B^- and C^+D^- . Ions A^+ and D^- may combine to form AD , and ions C^+ and B^- may form CB . In some instances there are no indications that the ions of the solution combine, this is true, for example, when dilute solutions of potassium chloride and sodium nitrate are mixed (page 405). In other instances, the reaction between two ions occurs to at least a significant extent; in still others, it is almost complete in the sense that the ions are removed almost completely from the solutions. The extent to which they are removed depends upon (1) the solubility of the compound that they form, and (2) its degree of ionization, if it is soluble. Let us consider three specific examples.

30 Reactions that Form a Slightly Soluble Gas

A solution of sodium carbonate and hydrochloric acid contains hydrogen, chloride, sodium, and carbonate ions. Either positive ion (H^+ or Na^+) might be expected to combine with either negative ion (Cl^- or CO_3^{2-}). Sodium ion does not combine with either negative ion, however, because both sodium chloride and sodium carbonate are soluble salts and are completely ionized. Hydrogen ion will not combine with chloride ion, because hydrochloric acid is a highly ionized electrolyte, but it will combine with carbonate ion to form, first, the weakly ionized bicarbonate, HCO_3^- , ion and then, to a lesser extent, to form carbonic acid, H_2CO_3 . This acid is unstable and decomposes into water and carbon dioxide, which is only slightly soluble and consequently escapes. If carbon dioxide did not escape, or if carbonic acid were stable, we should expect the following equilibrium to be set up

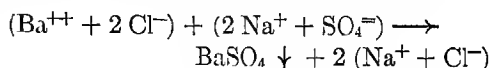


The escape of carbon dioxide from the solution disturbs this equilibrium and results, eventually, in almost complete removal of the carbonate ion, provided that a sufficient quantity of hydrochloric acid is added to convert all of the carbonate ion into carbonic acid. So long, of course, as any carbon dioxide remains in the solution, there will be small concentrations of both bicarbonate and carbonate ions.

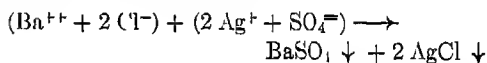
31 The Formation of a Slightly Soluble Solid

A solution of barium chloride contains barium and chloride ions. A solution of sodium sulfate contains sodium and sulfate ions. When these two solutions are mixed, we might assume that the ions will remain together without any visible change, as in the solution of sodium nitrate and potassium chloride. But something does happen in this mixture. A white solid, which can be identified as barium sulfate, is precipitated from the solution. Barium sulfate is only slightly soluble in water; about 0.00001

gram-molecular weight dissolves in one liter at $20^\circ C$. It is possible, therefore, for a solution to contain only small concentrations of barium and sulfate ions. When they are mixed, these ions form crystals of barium sulfate, leaving only as many ions in the solution as are required to produce saturation. The removal of these ions from the solution, therefore, is almost complete. Sodium and chloride ions remain in the solution, since sodium chloride is soluble.



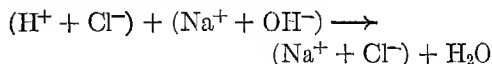
In some reactions, both sets of ions may be removed from the solution. This happens when both substances which the ions may form are slightly soluble. This type of double decomposition is represented by the reaction of barium chloride and silver sulfate.



If barium chloride and silver sulfate are added in equal molecular quantities, the liquid finally remaining after the precipitation of the two products contains almost nothing but water, since the solubilities of both products are of the order of 1×10^{-5} gram-molecular weight per liter.

32. The Formation of Slightly Ionized Substances

When HCl and $NaOH$ are placed in the same solution, the solution contains, at first, four ions — H^+ , Cl^- , Na^+ , and OH^- .



The sodium and chloride ions do not combine, of course, since sodium chloride is soluble and completely ionized, but the situation for hydrogen and hydroxyl ions is very different. Water is only slightly ionized; to have a solution containing, simultaneously, a large number of each of these ions is to have, obviously, an impossible condition — an abundant supply of the ions of a substance that can produce very few ions. We have learned (page 444) that the product of the concentrations of these two ions at

25° cannot exceed 1×10^{-14} . If greater concentrations than correspond to this product are brought together, there can be but one result. The ions will combine to form molecules of water until the ionic concentrations remaining yield this product. The small value of the product, $[H^+] \times [OH^-] = 1 \times 10^{-14}$, indicates just how small the concentrations of H^+ and OH^- must become. The reaction of these two ions, therefore, is almost complete.

Whenever the ions of any weak electrolyte are brought together in solution, they react to form the non-ionized molecules of the electrolyte until equilibrium is established. Since the ionization constants of all weak electrolytes are small fractions, this means that many of the ions are converted into molecules before equilibrium is established. Thus, when hydrogen ions and acetate ions are brought together, they combine to form molecules of acetic acid until, at equilibrium, the product of the ionic concentrations divided by the concentration of non-ionized acetic acid is 0.000018.

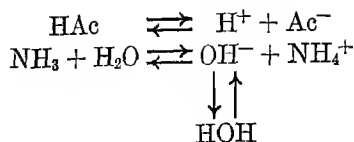
$$\frac{[H^+] \times [Ac^-]}{[HAc]} = 0.000018.$$

Because of the small size of this constant, these ions combine to a considerable extent. The same is true for the ions, NH_4^+ and OH^- , H^+ and S^{2-} , and the ions of other weak electrolytes.

33 Neutralization

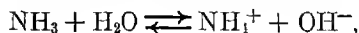
When a strong acid reacts with a hydroxide, such as NaOH, the only reaction that occurs is the combination of hydrogen and hydroxyl ions to form molecules of water. We speak of this reaction as the neutralization of the acid and the base. With weak electrolytes the changes that occur are different only in that these substances are slightly ionized and their reactions, consequently, are less nearly complete. Let us consider the neutralization of acetic acid in an aqueous solution by ammonium hydroxide, which may be regarded as a solution of

ammonia containing ammonium and hydroxyl ions



Starting with a solution of acetic acid, the concentration of the hydrogen ion is greater than it is in pure water ($pH < 7$). The extent to which it is greater depends upon two factors: (1) the number of molecules of the acid per liter, and (2) the ionization constant of the acid. As the base is added, the concentration of hydroxyl ion increases, and hence, since the product $[H^+] \times [OH^-]$ must always be 1×10^{-14} , the concentration of hydrogen ion decreases as the two ions combine to form molecules of water. This decrease in the hydrogen ion's concentration disturbs the equilibrium between acetic acid and its ions, consequently, more molecules of acid ionize to restore equilibrium. This change, in turn, leads to an increase in the concentration of hydrogen ion and prevents the establishment of the equilibrium involving the ions of water, $[H^+] \times [OH^-] = 1 \times 10^{-14}$. More molecules of water are formed, whereupon more molecules of acid ionize, and so on.

At the same time, the equilibrium,



is disturbed by the removal of OH^- ions to form water, and more molecules of ammonia are converted into ammonium ions. If a sufficient quantity of ammonium hydroxide is added, the acid can be almost completely converted into water and acetate ions, at the same time, most of the hydroxyl ions are converted into water, leaving ammonium ions in the solution. Since acetic acid and ammonium hydroxide are approximately equally ionized, a solution in which equivalent quantities of these two substances are mixed will contain approximately the same concentrations of hydrogen and hydroxyl

ions; the solution will be almost exactly neutral and its pH will be almost exactly 7

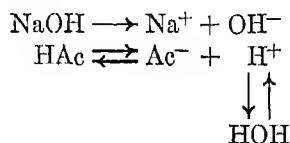
We must remember, however, that both acetic acid and ammonium hydroxide are weak electrolytes. Since the solution resulting from the neutralization of one by the other contains some hydrogen and some hydroxyl ion and large numbers of acetate and ammonium ions, we must assume that it also contains at least very small quantities of the non-ionized acid and ammonia. The ions of the acid must be in equilibrium with molecules of the acid, and ammonium and hydroxyl ions must be in equilibrium with molecules of ammonia and water. All of this means that the reaction between the acid and the base is not complete, and that the reverse reaction occurs to some extent

34. The pH of Solutions in Which Acids Have Been Neutralized by Bases

One more question remains to be answered. Are the concentrations of hydrogen and hydroxyl ions the same in all solutions in which an acid has been neutralized by adding an equivalent quantity of a base? Is such a solution neutral, acid, or alkaline? The answer depends upon the relative degrees of ionization of the acid and the base. If they are approximately equally ionized — as we have seen acetic acid and ammonium hydroxide to be — the solution will contain about the same concentrations of hydrogen and hydroxyl ions and will be, therefore, almost exactly neutral.

Let us consider the neutralization of acetic acid by the strong base, sodium hydroxide. When one liter of 1 N sodium hydroxide is added to a solution containing one gram-molecular weight of the acid per liter, a sufficient number of hydroxyl ions is added to react with all the hydrogen ions that this weight of the acid can supply. The solution containing the mixture, however, is not neutral, the concentrations of H^+ and OH^- are not each 1×10^{-7} and, if we add a suitable indicator, the color produced is not the color that the indicator should give for a

pH of 7. Rosolic acid, for example, which is red in a solution whose pH is above 7, gives a definitely red color to this solution. Even phenol red, which changes color at a pH of about 7.7, gives a red color, the color that it shows in an alkaline solution — one in which $[OH^-] > [H^+]$. The pH of this solution corresponds approximately to the transition range of phenolphthalein (8.3 – 9.5), and is, therefore, decidedly on the alkaline side of the neutral point. This effect is the result of differences in the degrees of ionization of sodium hydroxide and acetic acid.



Sodium hydroxide and sodium acetate are completely ionized, but there must always be an equilibrium between the ions and the molecules of acetic acid. Since some of the hydrogen ions must remain in molecules of the acid, instead of being free to combine with hydroxyl ions, the concentration of hydrogen ion must be less than that of the hydroxyl ion, and hence the solution is alkaline, although equivalent quantities of the acid and base have been mixed.

35. Standard Solutions and Titrations

A *standard solution* is one that contains a definite and known concentration of solute. A solution that contains a sufficient quantity of acid to supply one gram-ion of hydrogen per liter, for example, is a standard solution. Such a solution can be used to determine the concentration of sodium hydroxide in a solution of that substance. The solution of the acid is added to a definite volume of the solution of the base until the quantity of acid added is equivalent to the quantity of base, as shown by the change in color of a suitable indicator. The analysis of a solution by this procedure is called *titration*. The *end-point* of a titration is reached when chemically

equivalent quantities of acid and base have been mixed. The change in color of the indicator, which tells us when we have reached the end-point, should occur, therefore, at a pH that corresponds to the presence of equivalent quantities of the two substances, ideally, the change in color should occur at a pH of 7, although we shall soon see that, in practice, indicators that change colors at other pH values are sometimes more desirable.

One liter of a 1 N solution of sodium hydroxide and one liter of a 1 N solution of hydrochloric acid contain equivalent weights of hydroxyl and hydrogen ions, respectively. Hence a liter of one of these solutions requires by titration one liter of the other. A suitable indicator for this titration is one that gives an end-point when these two volumes have been mixed.

36. A Problem Involving Titration

The use of a standard solution in titration is illustrated by the following example.

Let us assume that we wish to determine the weight of hydrogen chloride in a liter of a solution of the acid, that is, we wish to know the normality

of the solution. A definite volume of the solution is measured out in a beaker from a burette, Figure 201, or a pipette, Figure 202. A few drops of the solution of an indicator are then added, and a standard solution of a base is next added from a burette until the change of color of the indicator shows that all of the acid has been neutralized.

If the sample of acid consists of 20 ml, and if 40 ml of normal sodium hydroxide solution is required for the neutralization, the solution of the acid is obviously twice as concentrated (2 N). If 20 ml of another solution of the acid is neutralized by 10 ml of normal sodium hydroxide solution, the concentration of the acid is 0.5 N, and so on.

It should be noted that the volume of a standard solution of a base that is required to neutralize a definite volume of a solution of an acid is *not* a measure of the relative strength of the acid. Equal volumes of normal acetic and hydrochloric acid contain the same number of ionizable hydrogen atoms, although the numbers of hydrogen ions existing in the two solutions at any one time are not the same. The titration of the acid with a standard solution of a base determines the *total possible acidity* and not the hydrogen ion concentration. The latter might be regarded as a sort of temporary acidity.

37. The Choice of Indicator in Titration

An acid can be said to have been neutralized by a base when chemically equivalent quantities of the two substances have been brought together. For each gram-equivalent weight of the acid there must be added one gram-equivalent weight of the base. This does not mean, however, that the pH of the mixture will be 7, because the solution containing chemically equivalent weights of the substances will usually not be exactly neutral. Strict neutrality will be attained only if the acid and base are ionized to the same extent (page 450). *Different indicators must be used with different types of acids and bases to determine when exactly equivalent quantities*

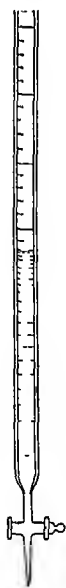


Figure 201
A Burette



Figure 202
A Pipette

of the two substances have been brought together. Given below are the pH values of the solutions resulting when equivalent quantities of different types of acids and bases are mixed, with the type of indicator most desirable for use in determining the end-point of the titration.

(1) Strong base and strong acid. The solution is almost exactly neutral, pH about 7. Use rosolic acid, litmus, neutral red, thymol blue, almost any indicator can be used. Methyl orange is often added. Care should be taken to exclude carbon dioxide, since this is a weak acid and would influence the concentration of hydrogen ion considerably.

(2) Strong base and weak acid. The solution is slightly alkaline (pH > 7). Use phenolphthalein or cresol red. The former is most often used.

(3) Strong acid and weak base. The solution is slightly acid (pH < 7). Use methyl orange, methyl red, or brom-phenol blue. The first is most often used.

(4) Weak acid and weak base. The solution is either acid or alkaline depending upon whether the acid or the base is stronger. No indicator works very well.

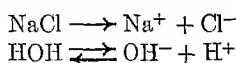
38 Hydrolysis

We might expect the solution of a salt, which is made by neutralizing an acid and a base, to be neutral. We must consider, however, the possible reactions that may occur between the ions of the salt and the ions of water. To the extent that such reactions occur, the salt is said to be *hydrolyzed*. Substances other than salts also hydrolyze. Thus, the halides of phosphorus react with water to form phosphorous acid and the hydrogen halides (page 347), although these compounds of phosphorus are not salts. Hydrolysis may be defined, therefore, as a double decomposition involving the ions of water and another substance, usually a salt.

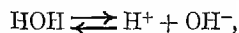
39 Examples of the Hydrolysis of Salts

Let us examine the reaction possibilities of the solutions of a few typical salts in water.

(a) Sodium Chloride (NaCl)

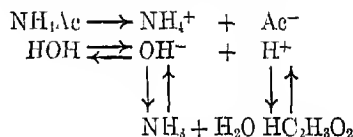


Both sodium hydroxide and hydrochloric acid are strong electrolytes, in dilute solutions, at least, the latter can be considered as completely ionized as the sodium hydroxide, which even in its solid state is composed of ions. Neither the hydrogen ions nor the hydroxyl ions are removed from this solution to form molecules of a weak acid or a weak base, a slightly soluble solid, or a gas, and hence, the equilibrium,



is undisturbed, and the concentrations of hydrogen and hydroxyl ions remain the same in a solution of sodium chloride as they are in pure water. The ions of the salt react with neither ion, and hence this salt is not noticeably hydrolyzed, and its solution is neutral.

(b) Ammonium Acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$)

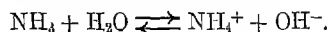


Both acetic acid and ammonium hydroxide are weak electrolytes. Although water is very slightly ionized, it does produce small concentrations of its ions in the solution, and ammonium acetate, of course, produces large concentrations of ammonium and acetate ions. At the time that the salt dissolves, the solution therefore contains the ions of acetic acid but no non-ionized molecules. This is an unstable and impossible condition, since this acid is only slightly ionized. Hence its ions combine to form molecules of the acid until the conditions of the equilibrium are fulfilled.

$$\frac{[\text{H}^+] \times [\text{Ac}^-]}{[\text{HAc}]} = 0.000018$$

Since this constant is small, and since the concentration of the acetate ion is very great, the concentration of acetic acid (molecules), also, must become fairly large before equilibrium can be established. For this to happen, the concentration of hydrogen ion must become small, since there are no molecules of acid in the beginning.

Likewise, hydroxyl ions are removed from the solution by reacting with ammonium ions to establish equilibrium in the reaction



Now the apparent degrees of ionization of ammonium hydroxide and acetic acid are about the

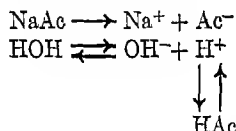
same, hence equal concentrations of H^+ and OH^- ions are removed from the solution to form about the same number of molecules of acetic acid and ammonia. As the ions are thus removed, more molecules of water ionize to maintain the equilibrium required by the equation

$$[H^+] \times [OH^-] = 1 \times 10^{-14},$$

but the solution remains almost exactly neutral.

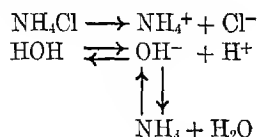
For the reasons given above, the hydrolysis of a salt of a weak acid and a weak base¹ is at least fairly extensive. The extent to which the reaction is completed depends upon the extent to which the acid and base are ionized, because this condition determines, in turn, the extent to which the ions of the salt and those of water combine to form non-ionized molecules of the acid and base. The solution of ammonium acetate is practically exactly neutral, because the acid and base are ionized to approximately the same degree. This means that the hydrogen and hydroxyl ions are withdrawn from the solution to about the same extent.

(c) *Sodium acetate* ($NaC_2H_3O_2$).



Since sodium hydroxide is much more highly ionized than acetic acid, the solution of sodium acetate shows an alkaline reaction ($pH > 7$). Hydrogen ions are converted into molecules of acetic acid until the equilibrium for the ionization of this acid is established. This disturbs the ionization equilibrium of water, and more molecules of this substance ionize. Since the hydroxyl ions are not removed, they accumulate, thus reducing the concentration of hydrogen ion in accordance with the requirement that $[H^+] \times [OH^-]$ must be equal to 1×10^{-14} . Sodium acetate is hydrolyzed to a greater extent than sodium chloride but less than ammonium acetate.

(d) *Ammonium Chloride* (NH_4Cl)



¹ The solution of ammonia in water is regarded as a weak base, because the ammonia reacts with water to form relatively few ions.

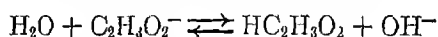
The hydroxyl ions are removed from the solution to establish equilibrium between the ions of NH_4^+ and OH^- , on the one hand, and molecules of water and ammonia on the other. Hence, more water ionizes, and the hydrogen ions, which are not removed from the solution, accumulate to give the solution a decidedly acidic character. Ammonium chloride is hydrolyzed to about the same extent as sodium acetate.

40 The Extent of Hydrolysis

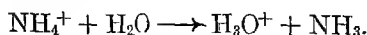
Hydrolysis is one of those reactions between ions (page 449) that occur because of the formation of slightly ionized substances. Those salts are most highly hydrolyzed, therefore, which form the least ionized acids and bases. If both are weak, hydrolysis is more extensive than if one is strong. If one is an insoluble solid or a gas, this also causes the hydrolysis to be more pronounced.

41. Hydrolysis of Salts Explained in Terms of the Bronsted Concept

According to the Bronsted concept, the hydrolysis of a salt involves simply the protolytic reaction (transfer of a proton) between an acid and a base. The acid is water and the base is the anion of the salt in solutions of salts such as sodium acetate:



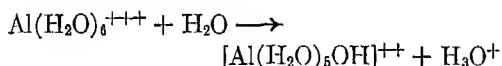
The hydrolysis of sodium acetate would be much more nearly complete except for the fact that OH^- is a stronger base than $C_2H_3O_2^-$, and hence OH^- has a stronger tendency to attract and hold the proton, thus forming HOH , than $C_2H_3O_2^-$ has in forming $HC_2H_3O_2$. Some protons are transferred from water to acetate ions, however, and such changes produce additional OH^- ions, thus causing the solution of the salt to be alkaline ($pH > 7$). In the solution of a salt of a weak base and a strong acid, e.g., ammonium chloride, NH_4Cl , hydrolysis results from the reaction of the cation, NH_4^+ , of the salt with water



Here again, hydrolysis is limited by the fact that ammonia is a stronger base than water, it reacts with protons and holds them more firmly than water. Because the reaction does occur to some extent, additional H^+ ions (actually, H_3O^+ ions) are produced, and the solution is acidic in properties ($pH < 7$).

42. Hydrolysis of Hydrates

The salts of many of the metals and the anions of strong acids form solutions that are slightly acidic. It is believed that this condition is the result of reactions of hydrated ions with water. For example, the hydrated aluminum ion may react with water as follows

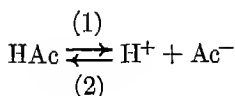


Solutions of cupric chloride, $CuCl_2$, and cupric sulfate, $CuSO_4$, and similar salts are acid in reaction for the same reason.

43. The Common Ion Effect

The common ion effect is observed when one of the ions of a weak electrolyte is added in excess to the solution. When this is done, the concentration of the other ion is decreased, and the concentration of the non-ionized (molecules) of the electrolyte is increased. *The general effect, therefore, is to reduce the percentage of ionization of the electrolyte.*

Let us illustrate by using again a solution of acetic acid. The common ion effect will be observed if sodium acetate is added to the solution, the acetate ion is the common ion. We shall assume that equilibrium had been established before the sodium acetate was added.



The salt is ionized completely, and its addition, therefore, considerably increases the concentration of the acetate ion. Since the

speed of reaction (2) is increased by this change of concentration, while that of reaction (1) is not, molecules of acetic acid will be produced temporarily in greater numbers than they ionize. Finally, however, as the ions are withdrawn and the number of non-ionized molecules increases, the two speeds will become equal again, and equilibrium will be established once more. For the new equilibrium, the concentration of hydrogen ion will be less than for the first, and the concentrations of acetate ions and acetic acid molecules will be greater.

To take a definite example, let us assume that we have, at first, a tenth-normal solution of the acid. Since acetic acid is 1.34 per cent ionized in this solution, the concentration of each ion is 0.00134 gram-ion per liter.

$$\frac{0.00134 \times 0.00134}{0.0987} = 0.000018$$

Let us now add solid sodium acetate to the extent of 0.1 gram-molecular weight per liter. We shall assume that the salt is completely ionized, hence we have added 0.1 gram-ion of acetate. The total concentration of the acetate ion is now $0.00134 + 0.1 = 0.10134$ gram-ion per liter. To restore equilibrium a certain number of hydrogen ions and an equal number of acetate ions combine to form molecules of acetic acid. Let us call this number x . The equation for the new state of equilibrium, therefore, is

$$\frac{(0.00134 - x)(0.10134 - x)}{(0.0987 + x)} = 0.000018$$

Solving this equation for x we find it to be 0.00132. The concentration of the hydrogen ion is reduced by the sodium acetate to $0.00134 - 0.00132 = 0.00002$ gram-ion per liter.

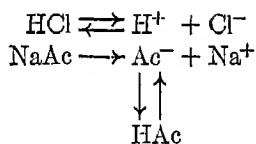
44. The Effect of Different Ions upon the pH or Acidity of Solutions

The pH of the solution of any weak acid is always increased by the addition of a salt of the acid, as for example the addition of sodium acetate to a solution of acetic acid. This effect means that the percentage of the acid that is ionized is decreased by the addi-

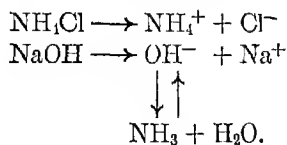
tion of the salt, and that the acid appears to be weaker than it is in a solution containing only the acid and water

We can show that an excess of ammonium or hydroxyl ions decreases in a similar manner the extent to which ammonia and water react to form these two ions. Thus, a solution of ammonium hydroxide in which there is also dissolved an ammonium salt, such as ammonium chloride, has a lower pH than a solution containing nothing but ammonium hydroxide

Solutions of strong acids and strong bases, such as HCl and NaOH, are not appreciably affected by the addition of the salts of the acid or base. The concentration of hydrogen ion in a solution of HCl to which an acetate, or the salt of any weak acid, is added, however, is much smaller than it is in a solution to which no salt has been added. The reason for this effect is apparent from the following equation



The addition of ammonium chloride likewise reduces the concentration of hydroxyl ion in the solution of a strong (hydroxide) base



When ammonium and hydroxyl ions are mixed, they must react to form ammonia and water until equilibrium is established. Since the concentration of the ammonium ion is high, the concentration of the hydroxyl ion is reduced considerably, and hence the concentration of the hydrogen ion must be increased correspondingly, by the further ionization of water, so that the product $[\text{H}^+] \times [\text{OH}^-]$ may be kept at its constant value of 1×10^{-14} .

45. Buffered Solutions

The pH of a solution containing a relatively high concentration — let us say 0.1 N — of acetate ion is not much affected by the addition or removal of small quantities of an acid. The ionization constant, 0.000018, of acetic acid must be maintained, and this means that the concentration of H^+ must remain small as long as the concentration of Ac^- is large. If a small quantity of a strong acid is added, the hydrogen ions and acetate ions react to restore equilibrium, which will require that the concentration of H^+ be reduced to almost the same small value as before the acid was added. If this should not happen, the product $[\text{H}^+] \times [\text{Ac}^-]$ would be too large to give the correct value of the ionization constant. Wide variations in the concentration of H^+ are thus prevented by the use of a relatively high concentration of Ac^- ion.

For similar reasons the concentration of hydroxyl ion cannot vary greatly in a solution of ammonium hydroxide that contains a high concentration of ammonium chloride. In general, we may say that the pH of any faintly acid or alkaline solution tends to remain practically constant, regardless of other ions that may be added, if the solution contains the proper salt, that is, the salt of a weak acid for faintly acid solutions and the salt of a weak base for a faintly alkaline solution. These salts are said to buffer the solution and are called *buffer salts*.

The principle of buffer action has many important applications. One of the most important of these is the buffering effect of certain salts, such as phosphates, in the blood. The pH of the blood is maintained at about 7.35. Certain processes in the body tend, however, to alter this value. The withdrawal of hydrogen ion to form the hydrochloric acid of the gastric juice is a process of this kind. Another is the oxidation of sugars and other substances in the body. This reaction results in the formation of carbon dioxide which accumulates in the blood, unless the respiratory organs are able to remove it as rapidly as it forms. Since carbon dioxide forms an acid in

solution, its accumulation would lead to a decrease in the pH. This decrease would be more pronounced and might lead to serious effect if buffer salts did not act to maintain a more nearly constant hydrogen ion concentration. If the buffer salts cannot prevent a slight increase in acidity, the pH drops and this leads to a stimulation of the nerve centers that control the rate of respiration. The rate of respiration is increased in order that the excess of carbon dioxide may be expelled. As soon as the pH of the blood has returned to its normal value, the rate of respiration also becomes normal again.

Not only does buffer action play an important part in the blood, but we know that many other biological processes in solutions occur in the presence of certain buffer salts. The digestion of different foods must occur in solutions that are buffered to a fairly definite hydrogen ion concentration.

46. Ionic Equilibria in Saturated Solutions

A solution which is saturated with a substance at a definite temperature contains a definite concentration of that substance. Let us consider the solution of a slightly soluble salt, such as silver chloride, that has been prepared by mixing the solid salt with pure water. Crystals of silver chloride, AgCl , contain equal numbers of silver and chloride ions, and hence, for each chloride ion in a saturated solution prepared in the manner described, there is one silver ion. Furthermore, the saturated solution of silver chloride, at a definite temperature, always contains the same concentration of the salt. Therefore, it is evident that the concentrations of the ions are *equal* and *constant*. The product of the concentrations is also constant:

$$[\text{Ag}^+] \times [\text{Cl}^-] = \text{Constant}$$

The concentrations of the two ions, however, are not always the same in saturated solutions prepared in other ways. If the concentration of chloride ion is increased by the addition of sodium chloride, the solubility of silver chloride decreases. A saturated solution, under this condition, contains less silver ion and more chloride ion than a

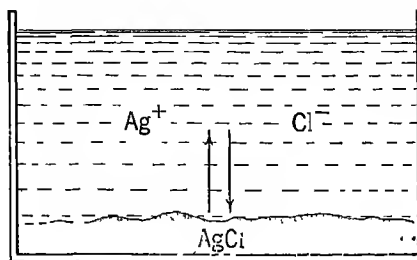


Figure 203

The solubility product of silver chloride (at a given temperature) is the product of the concentrations of the silver and the chloride ions in a saturated solution.

saturated solution made by dissolving silver chloride in pure water. In the presence of sodium chloride, the decrease in the concentration of silver ion is proportional to the increase of chloride ion. The product of the ionic concentrations $[\text{Ag}^+] \times [\text{Cl}^-]$ therefore remains unchanged. The product of the ionic concentrations in a saturated solution of a substance, like silver chloride, that contains only univalent ions, is called the *solubility product* of the substance. The name is quite appropriate, because the numerical value of the product depends essentially upon the (molar) solubility of the compound. The principle of the solubility product applies only to compounds (composed of ions) that are slightly soluble and whose saturated solutions, therefore, are very dilute.

In silver chloride, each ion has a unit charge (Ag^+ and Cl^-). In silver sulfate, however, two silver ions, each carrying one unit of positive charge, are required to form the chemical equivalent of one sulfate ion, SO_4^{2-} . A saturated solution prepared by dissolving silver sulfate in pure water contains, therefore, twice as many silver ions as sulfate ions. Experimentally, we can show that the solubility of silver sulfate, and hence the concentration of sulfate ion in a saturated solution, decreases in a manner that is directly proportional to the square of the concentration of silver ion. The equation for the solubility product of silver sulfate may be written as

$$[\text{Ag}^+]^2 \times [\text{SO}_4^{2-}] = \text{Solubility Product}$$

We should therefore extend our definition of the solubility product to state that *it is the product of the ionic concentrations, in a saturated solution, and is obtained by taking as a factor the concentration of each ion as many times as that ion appears in the formula of the substance*

Calculations of Solubility Product

Let us calculate the solubility product of silver chloride. The solubility of silver chloride is 0.00001 gram-molecular weight per liter at 18°. Since the molecule does not exist, this means really that $0.00001 \times$ (the combined gram-atomic weights of Ag^+ and Cl^- ions) dissolves in one liter. Since the two ions are produced in equal numbers, the saturated solution contains 0.00001 gram-ion each of Ag^+ and Cl^- per liter. The solubility product, therefore, is

$$0.00001 \times 0.00001 = 0.0000000001, \text{ or } 1 \times 10^{-10}$$

The solubility of magnesium hydroxide is 0.0002 gram-molecular weight per liter. Assuming that this substance is completely ionized, the concentration of the magnesium ion (Mg^{++}) is 0.0002 gram-ion per liter. But the concentration of the hydroxyl ion is twice this amount (0.0004 gram-ion per liter), since two hydroxyl ions are formed for each magnesium ion. The solubility product, therefore, is equal to

$$0.0002 \times (0.0004)^2 = 0.000000000032, \text{ or } 3.2 \times 10^{-11}$$

The solubility products of other substances are given in Table II, Appendix

47. Conditions Determining the Extent to Which an Ion can be Removed from a Solution by Precipitation

A substance begins to precipitate as soon as the product of the concentrations of its ions exceeds its solubility product, and the total quantity that precipitates depends upon the extent to which the product of the concentrations of the ions exceeds the solubility product. Tem-

perature, of course, has an effect, because the solubility, and hence the solubility product, changes as the temperature changes

The presence of other ions also alters the value of the solubility product of a compound, because such ions produce electrostatic forces that must inevitably have an influence upon the motion of the ions of the compound. This effect may change considerably the concentrations of the ions that must be present to make the rates of solution and precipitation, or crystallization, equal.

Consider, for example, the precipitation of silver chloride when one gram-ion each of silver and chloride ions are brought together in one liter of an aqueous solution. Silver chloride must precipitate until the product of the concentrations of its ions is 1×10^{-10} , or each concentration is reduced to 0.00001 gram-ion per liter. This means that $1 - 0.00001$ or 0.99999 gram-molecular weight of AgCl will precipitate. This quantity varies slightly, of course, with the temperature. Unless the product of the ionic concentrations of the silver chloride solution exceeds 1×10^{-10} , no precipitate will form. For example, no precipitate forms when 0.1 gram-ion of silver is placed in a solution containing 1×10^{-11} gram-ion of chloride ion per liter, because $0.1 \times 1 \times 10^{-11} = 1 \times 10^{-12}$, and this product is smaller than 1×10^{-10} . This solution of silver chloride is not saturated.

48. How Can an Ion Be Most Completely Precipitated?

Let us say that we wish to remove silver ion as completely as possible from a solution by precipitating it as silver chloride. Since $[\text{Ag}^+] \times [\text{Cl}^-]$ in a saturated solution must be 1×10^{-10} , at 20°, it is obvious that the concentration of the silver ion in such a solution depends upon the concentration of the chloride ion, and that it decreases as the latter increases. If we wish to leave as little silver ion as possible in the solution — or precipitate as much of it as possible — we must make the chloride ion's concentration as great as conditions allow. For example, a solu-

tion that contains 1 gram-ion per liter of Cl^- can contain only 1×10^{-10} gram-ion of Ag^+

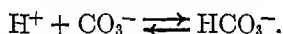
$$1 \times [\text{Ag}^+] = 1 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{1 \times 10^{-10}}{1}$$

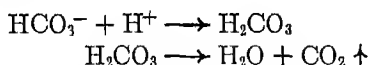
If the concentration of the chloride ion is 0.001 gram-ion per liter, then the concentration of the silver ion must be 1×10^{-7} for a saturated solution, and so on

49. The Influence of Hydrogen Ions upon the Precipitation and Solution of Calcium Carbonate

Let us consider the effect of the presence of hydrogen ions upon the precipitation of the carbonate of calcium. A solution containing sodium carbonate and calcium chloride will ordinarily yield a precipitate of calcium carbonate, since the solubility product of this substance is small (1.69×10^{-6}). In the presence of an acid, however, the following ionic reactions reduce the quantity of calcium carbonate that will precipitate.



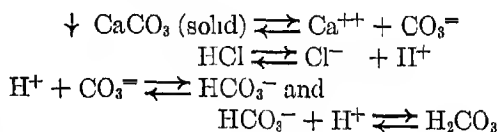
In the presence of a sufficient concentration of hydrogen ion, the following reactions also occur



Even if the reaction proceeds no further than to form bicarbonate ion, the concentration of carbonate ion is considerably reduced, because the bicarbonate ion is slightly ionized. Although the concentration

product of the carbonate and calcium ions may still be large enough to exceed the solubility product of calcium carbonate, certainly it cannot exceed it as greatly as it would in an acid-free solution, and hence a smaller quantity of calcium carbonate will precipitate. If sufficient acid is added, the concentration of the carbonate ion will be reduced to such a low value that the solubility product of calcium carbonate cannot be exceeded. No precipitate forms when this happens.

Consider, also, the changes that occur when an acid is added to a saturated solution of calcium carbonate in equilibrium with the solid (Figure 204)



Before the acid is added, the product of the concentrations of calcium and carbonate ions is equal exactly to the solubility product (1.69×10^{-6}), since the solution is saturated. The addition of the acid supplies hydrogen ions, which react with the carbonate ions, thus reducing their concentration, and causing the product of the ionic concentrations of the solution to fall below the solubility product. Since the solution is no longer saturated, more calcium carbonate dissolves to re-establish the saturated condition of the solution. If sufficient acid is added, all of the precipitate can be made to dissolve.

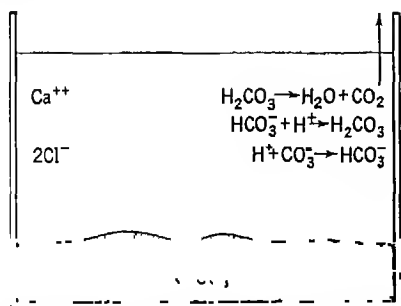


Figure 204. The Solubility of Calcium Carbonate in a Solution Containing Hydrochloric Acid

50. The Effect of Ammonium Ion upon the Precipitation of Magnesium Hydroxide

The effect of ammonium chloride upon the precipitation of a slightly soluble hydroxide, such as magnesium hydroxide, is explained by Figure 205. The addition of a large excess of ammonium ions reduces the available concentration of hydroxyl ions, because the two ions react to form ammonia and water. When this happens, the solubility product of magnesium hydroxide cannot be

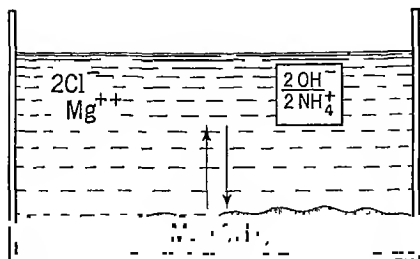


Figure 205 The Solubility of Magnesium Hydroxide in a Solution Containing Ammonium Chloride

exceeded as greatly as it might be in a solution containing no ammonium ion

$$[\text{Mg}^{++}] \times [\text{OH}^-]^2 = K_{sp}$$

Or if a precipitate of magnesium hydroxide has already been formed, it tends to dissolve in the solution of ammonium chloride, which renders the solution unsaturated by reducing the concentration of the hydroxyl ions

51. The Effect of Hydrogen Ion upon the Precipitation of Metallic Sulfides

In qualitative analysis some of the cations (metals) are separated from others by the precipitation of their sulfides. A solution containing the metallic ions is treated with hydrogen sulfide. Although this acid is very slightly ionized, its saturated solution contains a sufficient concentration of sulfide ions to cause the solubility products of the sulfides of many of the metals to be exceeded (see Appendix). If an acid, such as HCl, is added the concentration of the sulfide ion is reduced

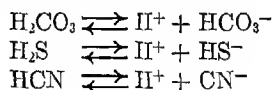


If the concentration of the hydrogen ion is increased, the concentration of the sulfide ion will be reduced a corresponding amount in order that the equilibrium condition may be maintained. If the concentration of the sulfide ion is reduced to just the right amount, it will be possible to exceed the solubility products of the least soluble sulfides (HgS , CuS , As_2S_3 , PbS , Sb_2S_3 , Bi_2S_3 , and SnS) without exceeding the solubility products of

the more soluble sulfides (FeS , ZnS , MnS , CoS , and NiS). We assume, of course, that the concentrations of the cations are approximately equal. In this manner it is possible to precipitate mercuric and cupric sulfides, for example, without precipitating zinc and manganese sulfides at the same time. After the removal of the first sulfides by filtration, the others may be precipitated from the filtrate by making this solution alkaline by adding ammonium hydroxide and again treating with hydrogen sulfide. The addition of hydroxyl ions reduces the concentration of the hydrogen ion and thus, indirectly, increases the concentration of the sulfide ion. It becomes possible, therefore, to exceed the larger solubility products of the more soluble sulfides, and these will then precipitate.

Review Exercises

- From the data concerning the percentages of ionization of different acids (page 437), calculate the concentration of H^+ in 0.1 M solutions of HCl, HAc, and HCN. Assuming that only the first stage of ionization occurs, make a similar calculation for H_2S , H_2CO_3 , and H_3PO_4 , if the concentrations are 0.1 M.
- From the data obtained in (1) and from page 437, calculate the ionization constants for the reactions



Assume 0.1 M solutions in each case

- Assuming that a solution of acetic acid contains molecules of the acid in equilibrium with the ions, H^+ and Ac^- , explain what will happen if you add (1) NaOH (solid), (2) NaAc (solid), (3) water, (4) HCl, (5) NaCl (solid).
- If you have a solution of ammonium hydroxide in which the molecules of ammonia and water are in equilibrium with the ions, what would happen if you added (1) HCl, (2) NH_4Cl (solid), (3) NaOH (solid), (4) water, (5) NaAc (solid), (6) NaCl (solid)?
- What is the concentration of OH^- ion in a 0.1 N solution of ammonium hydroxide? What is the concentration of H^+ ion in the

- same solution? What is the pH of the same solution?
- 6 Which of the following substances will give an acid reaction, and which will give an alkaline reaction when dissolved in water? Na_2S , KAc , CaCl_2 , $(\text{NH}_4)_2\text{SO}_4$, K_2CO_3
 - 7 In view of the fact that oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is a relatively weaker acid than HCl , explain why calcium oxalate will dissolve in a solution to which HCl is added
 - 8 Explain the advantage of using different indicators in titrating solutions of different acids and bases
 - 9 Suggest one reason why barium sulfate (BaSO_4) does not dissolve in a solution to which HCl has been added, while barium carbonate (BaCO_3) does
 - 10 Explain why magnesium hydroxide is not precipitated as completely in the presence of NH_4Cl as in its absence
 - 11 What is incorrect in the following statement? Phosphoric acid is a stronger acid than sulfuric, because it contains three replaceable atoms of hydrogen per molecule while sulfuric has but two
 - 12 Silver nitrate was added in excess to 100 ml of a solution of HCl . The precipitated AgCl was filtered, dried, and weighed. The precipitate weighed 2.6 g. How much HCl was present in one liter of the original solution? What was the normality of the solution?
 - 13 15 ml of a solution of H_2SO_4 is completely neutralized by 32 ml of a solution of 0.5 N NaOH . What is the concentration of the solution of the acid in terms of (1) its normality and (2) the number of gram-molecular weights per liter?
 - 14 Define solubility product. What factors determine the size of the solubility product of a substance?
 - 15 What factor or condition determines the quantity of a substance that will precipitate from a solution in which the ions of the substance are brought together?
 - 16 Calculate the solubility products of BaClO_4 and $\text{Pb}(\text{OH})_2$ if their solubilities (at 18°) are 0.000015 and 0.0004 gram-molecular weight per liter, respectively. Assume that the solutes are completely ionized
 - 17 Using the solubility product principle, show why less lead hydroxide is precipitated in the presence of (1) NH_4Cl and (2) HCl .
 - 18 How does the concentration of the sodium chloride solution added to a solution of silver nitrate in precipitating AgCl affect the quantity of precipitate? Explain in terms of the solubility product principle
 - 19 What indicator could be used to distinguish between 0.1 N NaOH and 0.00001 N HCl , pure water and 0.01 N NH_4OH , and 0.00001 N NaOH and 0.001 N NaOH ?
 - 20 Would it be practical to use NaCl as a buffer against an acid solution? Explain
 - 21 Why is a solution of NaCl practically neutral while a solution of NH_4Cl is acid?
 - 22 Give in detail the method which you would use to determine the approximate pH of a solution of NH_4Cl
 - 23 The pH of a solution of an acid is 5. What is the concentration of H^+ in this solution? What is the concentration of OH^- ?
 - 24 Correct the following statements if they are false
 - (a) 10 ml of 1 N H_3PO_4 solution will neutralize one and one-half times as much NaOH as 10 ml of 1 N H_2SO_4
 - (b) H_3PO_4 is a stronger acid than HCl , because the same weight of sodium hydroxide can neutralize only one third as many milliliters of a 1 M solution of H_3PO_4 as it does of 1 M HCl
 - (c) Although phosphoric acid contains three ionizable hydrogen atoms per molecule, while sulfuric acid has but two, sulfuric acid is the stronger acid, because it has a higher apparent degree of ionization
 - 25 Which substances act as acids in each of the following (forward) reactions? Which substances act as bases in the reverse reactions?
 - (a) $\text{H}_3\text{O}^+ + \text{S}^{2-} \rightleftharpoons \text{HS}^- + \text{H}_2\text{O}$
 - (b) $\text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$
 - (c) $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$
 - (d) $\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}$
 - 26 What is the approximate pH of a solution that gives a blue color with brom-phenol blue, violet with sodium alizarin sulfonate, blue with brom-thymol blue, and yellow with thymol blue?
 - 27 If 20 ml of a solution of an acid is titrated against 1 N sodium hydroxide, and if 15 ml

- of the solution of the base is required, what is the normality of the acid?
- 28 What is the concentration of Ag^+ ion in a saturated solution of silver chloride, at 18° , if the concentration of chloride ion is 0.01 gram-ion per liter? How could such a solution be prepared?
- 29 Why does cupric sulfide, CuS , precipitate from a solution containing Zn^{++} , Cu^{++} , $\text{S}^{=}$, and H^+ ions, while zinc sulfide, ZnS , does not, although the concentrations of Zn^{++} and Cu^{++} are the same?
- 30 A colorless solution of acetic acid containing phenolphthalein turns pink as sodium carbonate is added. What does the change in color indicate? How was the condition causing this change produced?
- 31 Why does the pH of blood remain almost constant?
- 32 Why are there fewer sulfide ions per liter in a solution of H_2S when HCl is also present than in a solution of H_2S when no HCl is present?
- 33 Indicate whether the following statements are true or false
- The pH of a colorless solution containing phenolphthalein is greater than 7
 - The pH of a 0.1 N HCl solution is approximately 1
 - The pH of any solution containing an acid is greater than 7
 - The pH of a solution of sodium acetate is greater than 7
 - The pH of a solution of ammonium chloride is less than 7
 - As an acid is added to a solution of sodium hydroxide, the color of any indicator in the solution changes when equivalent quantities of acid and base have been mixed

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NITROGEN AND AMMONIA

Considerable doubt exists as to the nature of nitrogen. Though ranked among the simple non-metallic bodies, some circumstances have led to the suspicion that it is compound, and this opinion is warmly advocated by Sir H. Davy and Berzelius.

CHEMISTRY TEXT OF 1828

NITROGEN

1 Introduction

In 1772, Rutherford burned different substances, such as phosphorus and carbon, in vessels filled with air, and noticed that after combustion had occurred the air was different in several respects from ordinary air. It no longer supported combustion, and for this reason, Rutherford regarded it as air saturated with phlogiston. He also showed that the air in a small space that was occupied for some time by animals underwent a similar change. To study this air, he bubbled a sample of it through a solution containing an alkali, such as sodium hydroxide, and found that a portion — now called carbon dioxide — was absorbed. The final residue did not support life or combustion and, in general, was inactive as compared with ordinary air. Scheele later showed that the inactive gas produced by Rutherford was always present in air, and Lavoisier, who first recognized it as an element, gave it the name *azote*. Later, Chaptal suggested the name nitrogen for the element, because it was found to be a constituent of *niter*, a substance now known as potassium nitrate.

2 Sources of the World's Nitrogen Supply

Most of the world's nitrogen supply exists in the form of the free element. The atmosphere consists of almost 80 per cent of nitrogen by volume, or about 75 per cent by

weight, and the total quantity of it above every square mile of the earth's surface is about 20,000,000 tons. It is from this source that a large part of the nitrogen required to meet the world's needs is now obtained. The conversion of this nitrogen into useful compounds, such as ammonia, is sometimes referred to as the *fixation of nitrogen*. From the ammonia thus obtained, nitric acid, fertilizers, and other important products are manufactured. Nitric acid, in turn, is used to make many more. A considerable amount of ammonia is also obtained by the destructive distillation of coal, and, until fairly recent times, most of the nitric acid made in this country and elsewhere was manufactured by a process using sodium nitrate and sulfuric acid. The sodium nitrate required for this process was obtained from South America.

In the decay of organic material proteins are gradually changed into ammonia, nitrites, and nitrates by certain reactions that are influenced by the action of bacteria of several different kinds. Some of the ammonia escapes into the air. Some free nitrogen is also released during the decomposition of proteins; this also escapes and becomes a part of the vast store of nitrogen in the air. The nitrates resulting from the decay of nitrogenous material may accumulate, producing deposits of great value. Nitrates are very soluble and, therefore, such deposits

can form only under conditions where there is insufficient water to dissolve them and carry them away

An extensive deposit of sodium nitrate occurs in a desert region in the mountains along the Pacific coast of South America. Most of the deposit is in Chile. The beds vary in thickness from 8 inches to 14 feet and are found on the surface in a strip about 200 miles long and 2 miles wide. The origin of this deposit is not definitely known. Some theories attribute its formation to the oxidation of the excreta and remains of bird life or other organic materials. According to other theories, the sodium nitrate has been slowly leached from soil and rocks, and the solution has evaporated, leaving a residue of the salt. The material taken from the deposit is called *caliche*. This is leached with water, and a product that is richer in sodium nitrate than the crude material is obtained. This is called *Chile saltpeter*. Its production is controlled by the Chilean government, and a tax placed on its exportation is a most valuable source of income to that government. Somewhat similar nitrate deposits are found in caves in the central states of our own country. The saltpeter (KNO_3) of Mammoth Cave has been used in the manufacture of black gunpowder. Some caves in the limestone region of Indiana contain similar deposits. At least one of these is known as Saltpeter Cave. Cave-deposits of nitrate are the results of the decomposition of the remains and refuse of bats and other animals that inhabit these passages. The early supply of saltpeter came from India, where manure was allowed to decompose after mixing it with wood ashes. The latter supplied potassium carbonate, which reacted with the decomposition products of the manure to form potassium nitrate. This salt was separated from the valueless material by leaching the mass with water. The saltpeter was then allowed to crystallize from the solution. The product was used in the manufacture of black gunpowder.

Chile saltpeter finds widespread use as a constituent of fertilizers, in which it provides the necessary nitrogen content. It is also used in the manufacture of nitric acid. Various processes for producing nitric acid and other nitrogen compounds from the nitrogen in the air have made most countries more or less independent of the

South American supply of sodium nitrate, although the deposit is still a very valuable natural resource.

3 The General Importance of Nitrogen

Aside from its use in the manufacture of ammonia, nitric acid, and other compounds, the nitrogen of the air is of extreme importance and value to man and to all other forms of life. For example, it dilutes the oxygen, and therefore retards oxidation. Life, certainly, would be much different from what it is if the atmosphere were composed of pure oxygen; for one thing, it would probably be of much shorter duration. Not only would life be different, but the world would be a different place in which to live. The combustion of fuel in stoves and furnaces would be difficult to control, the corrosion of iron and steel would proceed so rapidly that their use would be impractical, and decay would also be greatly accelerated.

The nitrogen of the air indirectly supplies plants with one of their essentials, usually the element is obtained by plants in the form of compounds present in the soil, but the air is the indirect source. Over a long period of time, at least small quantities of these compounds are added to the soil as a result of reactions between nitrogen and oxygen, which combine under the influence of electrical discharges — lightning flashes — during thunderstorms. Certain plants can use the element more or less directly through the help of bacteria that inhabit nodules on their roots and convert free nitrogen into compounds that the plants require. From the compounds — compounds such as nitrates — thus made available to them, plants synthesize complex substances called *proteins*, which contain oxygen, carbon, hydrogen, and sometimes other elements in addition to nitrogen. The proteins made by plants may then serve as a part of the food supply of animals, which converts them into other proteins that are used in building up tissues or in other functions of their bodies. Familiar proteins include egg albumen, casein

(curds) of milk, and the gluten of wheat flour. The proteins of our diet are obtained from such foods as meats, eggs, milk, cheese, some vegetables, nuts, and cereals. Nitrogen is eliminated from the bodies of animals in the form of urea, $(\text{NH}_2)_2\text{CO}$, and other nitrogenous decomposition products found in urine. The element is necessary to the life of every plant and animal, it is required to build the protoplasm of every cell in their bodies. The proper functioning of the organs of our bodies is often a question of the proper metabolism of nitrogenous compounds. The human body contains about three pounds of nitrogen for one hundred pounds of weight.

Many of our manufacturing industries also depend to a very significant extent upon uses of the compounds of nitrogen. The most important of these compounds is nitric acid, which is used in manufacturing fertilizers, explosives, dyes, drugs, and many other materials.

4. Production of Nitrogen for Commercial Uses

For commercial uses nitrogen is obtained from the air. There is no natural compound that serves as an economical source of the element, because the principal problem of the nitrogen industry is to *make nitrogen compounds*. Hence, the production of the free element by decomposing a compound already made would be contrary to the primary purpose of the industry.

Nitrogen is produced by the fractional distillation (page 195) of liquid air (page 66). It is easily separated by this method from all other components of the air except argon and other inert gases that do not interfere in the use of nitrogen for most purposes.

5. Production of Nitrogen in the Laboratory

(1) Laboratory samples of nitrogen can be prepared by burning phosphorus, copper, hydrogen, carbon, or other combustible substances in air, thus removing the oxygen; the nitrogen obtained in this manner always

contains other substances, but a fairly satisfactory product can be obtained if the products of combustion are not volatile, as cupric oxide, or if they are gases that dissolve readily in water. The method shown in Figure 206 can be used when phosphorus is employed to remove the oxygen. When the phosphorus burns, the bottle is filled with a white smoke consisting of particles of phosphorus pentoxide, which soon dissolve in the water to form phosphoric acid, leaving a gaseous residue that is largely nitrogen. An experiment designed to remove oxygen from air by means of copper is shown in Figure 8, page 29. In this reaction the product, cupric oxide, is non-volatile and remains in the tube. Since only oxygen is removed, samples of nitrogen produced by any of these methods are never pure, they contain carbon dioxide, water vapor, and the inert gases. The carbon dioxide can be removed by passing the gas through a solution of sodium hydroxide, the water vapor can be condensed by cooling, but the removal of the inert gases is a difficult process that involves liquefaction, followed by distillation of the liquid to separate the elements that are present.

(2) Small samples of *pure* nitrogen are most readily prepared by heating ammonium nitrite (NH_4NO_2)

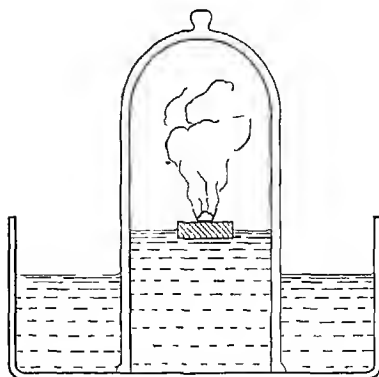
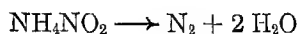
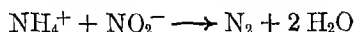


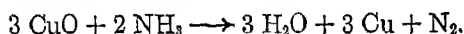
Figure 206. The Removal of Oxygen from a Sample of Air by the Combustion of Phosphorus

The water is easily condensed, leaving a very pure sample of nitrogen. Since ammonium nitrite is very unstable, some danger is involved in heating the pure, dry substance. In order to avoid this danger, the substance is usually prepared in solution from a mixture of sodium nitrite (NaNO_2) and ammonium chloride (NH_4Cl). When the mixture is heated slightly, the ammonium and nitrite ions react to form nitrogen and water:



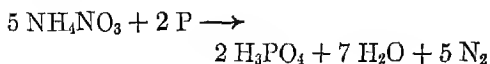
Heating must be carried out slowly, by immersing a vessel containing the mixture in another vessel filled with warm water, in order to prevent the reaction from becoming too rapid.

(3) Nitrogen can also be produced in small amounts by other reactions which involve the oxidation of nitrogen in compounds like ammonia, or the reduction of the nitrogen in compounds, such as the nitrates. Free nitrogen is formed, for example, when ammonia is passed over hot cupric oxide:



This reaction utilizes the oxidizing action of cupric oxide. Nitrogen is oxidized and copper is reduced.

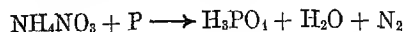
Nitrogen can also be produced from ammonium nitrate (NH_4NO_3), by the action of a vigorous reducing agent, such as phosphorus:



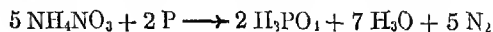
PRACTICE IN BALANCING EQUATIONS INVOLVING CHANGES IN VALENCE

Some of the reactions that we have just used in describing methods for the production of nitrogen are not very easily written as equations, unless we understand and use the method first described on page 356 for writing such equations. We shall show how three of these equations are balanced, in order that we may review the method and get further practice in using it.

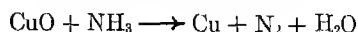
(a) The Reaction of Phosphorus with Ammonium Nitrate. Skeleton equation:



Each phosphorus atom changes its valence number from 0, for the free element, to 5, in phosphoric acid. Each nitrogen atom in the ammonium ion changes its valence number from -3 , in NH_4^+ , to 0, in N_2 . Each nitrogen atom in the nitrate ion changes from 5 to 0. For the two nitrogen atoms in the formula NH_4NO_3 , therefore, the total net change in valence number for nitrogen is -2 . In the balanced equation the changes in the valence numbers of the two elements must be the same, and we must use a sufficient number of phosphorus atoms and nitrogen atoms (in ammonium nitrate) to make this condition possible. The total change in the valence number of each element must, if it is to be the same for each, be the smallest common multiple of 2 and 5, which is 10. Now to get a total valence number change of 10 for phosphorus, we need two atoms, to do the same for nitrogen, we must use the formula, NH_4NO_3 , five times in the equation. We now know what we need to balance the left-hand side of the equation. The right-hand side is easy. Two atoms of phosphorus can form two molecules of H_3PO_4 , each of which contains one atom of phosphorus. Five nitrogen atoms in the five ammonium ions plus the five in the nitrate ions, or ten in all, will form five molecules of N_2 . There are also fourteen atoms of hydrogen on the left-hand side and seven atoms of oxygen that are not used in forming H_3PO_4 , these will form seven molecules of water. The complete equation, therefore, is

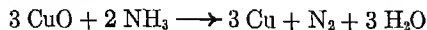


(b) The Reaction of Cupric Oxide and Ammonia. To balance this equation, we note that each copper atom changes in valence number from 2 to 0, each nitrogen atom changes from -3 to 0.

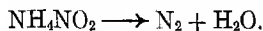


The smallest common multiple of 2 and 3 is 6, which must be the total change in the valence number of each element in the balanced equation. To get this we must use 3 atoms of copper and 2 of nitrogen, or 3 CuO and 2 NH_3 . The six atoms of hydrogen in 2 NH_3 show that three molecules of water are formed and, of course,

three atoms of copper and one molecule of nitrogen are set free



(c) *The Decomposition of Ammonium Nitrite*



Each nitrogen atom is set free in the decomposition of this compound. The nitrogen atom of the ammonium ion changes its valence number from -3 to 0, the one in the nitrite ion, from 3 to 0. Hence, the change in the valence of one kind of nitrogen (in NH_4^+) is exactly balanced by the change of the other (in NO_2^-).

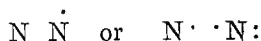
PROPERTIES OF NITROGEN

6. Physical Properties

Nitrogen is a colorless, odorless, and tasteless gas under ordinary conditions. Its boiling point under a pressure of 760 mm is -195.8° , and its freezing point is -209.9° . Its critical temperature is -147° . It is slightly less dense than air, which contains the heavier molecules of oxygen as well as those of nitrogen, under standard conditions, one liter weighs 1.2506 g. Nitrogen dissolves only slightly in water, under standard conditions, 100 ml of water dissolves about 2.3 ml of it.

7. Chemical Properties

The nitrogen atom contains five valence electrons, which are located in the second level. The molecule consists of two atoms united by one or more pairs of shared electrons. The following structures seem the most probable



The molecule is very stable, 172,000 calories being required to decompose a gram-molecular weight. This large quantity of energy accounts for the slight activity of the element, which shows very little tendency to form compounds with any other elements under ordinary conditions. It combines with many of the metals at elevated temper-

atures. When magnesium is burned in air, some of the metal forms the *nitride*, Mg_3N_2 . Other nitrides of metals are Ca_3N_2 , Li_3N , and AlN . The nitride of hydrogen is called ammonia and has the formula, NH_3 . At high temperatures, nitrogen combines with oxygen to form nitric oxide (NO). More active nitrogen is produced by subjecting the element to a high-voltage electrical discharge. This form of nitrogen probably consists of "excited" or activated atoms produced by the displacement of at least one valence electron to a level beyond the second (Figure 207). This form of nitrogen contains more chemical energy than ordinary nitrogen, and the displaced electron is more easily engaged in reactions, as, for example, in forming a pair with an electron from another atom. This active form of nitrogen combines readily with many elements, including sulfur and phosphorus, with which molecular nitrogen does not react.

Most nitrogen compounds are not produced directly from the element. Instead they are made from ammonia, nitric acid, or one of the oxides. In ammonia and in the nitrides of the metals, the element has a valence number of -3, which is explained by the five electrons in the atom's valence group or level. This group requires only three more electrons to make the eight needed for a stable structure, and hence the valence of the element in compounds such as ammonia, HN_3 , in which it completes the group of eight electrons by sharing three pairs of electrons with atoms of hydrogen or of some other element, is -3. The positive valence number of nitrogen may be 1, 2, 3, 4, or 5, as for example in the five oxides N_2O , NO ,

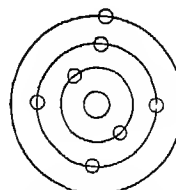


Figure 207. The Excited, or Active, Atom of Nitrogen

N_2O_3 , NO_2 , and N_2O_5 Nitrogen trioxide and nitrogen pentoxide are the anhydrides of nitrous, HNO_2 , and nitric, HNO_3 , acids, in which the valence numbers of nitrogen are 3 and 5, respectively. These acids and their salts — the nitrites and the nitrates — are among the most important inorganic compounds of the element. In the nitrite and nitrate ions, NO_2^- and NO_3^- , and in the oxides as well, atoms of nitrogen form covalent bonds with oxygen.

8. Uses of Nitrogen and Its Compounds

The high degree of stability possessed by molecular nitrogen results in a tendency of many compounds of the element to decompose, liberating the free element. Many of these break up following percussion and are therefore used as explosives. Their use for such purposes depends upon the expansion that accompanies the decomposition. The compounds are usually solids. The products of the explosion are gases, which often include free nitrogen. The change from the solid to the gaseous state, together with the expansion of the gas that accompanies the liberation of heat and rise in temperature as the compound decomposes, results in a tremendous increase in volume. If this occurs rapidly enough, other substances — air, etc. — are forced out of the way with "explosive violence." One of the simplest explosive compounds of nitrogen consists of nitrogen triiodide combined with ammonia, $\text{NI}_3 \cdot \text{NH}_3$. This substance may be exploded by a slight jar. It is too sensitive to percussion to be of any practical value as an explosive. Important explosives are made by the action of nitric acid upon glycerine, toluene, cellulose, phenol, and the like.

Nitric acid is also used in enormous quantities to produce fertilizers, drugs, dyes, photographic films, and lacquers. Ammonia, in addition to its use in limited quantities in the household and in the chemical laboratory, is used in the manufacture of fertilizers. Much of it is also converted into nitric acid. The most important use of free nitrogen,

therefore, is in the synthesis of these two important chemicals — ammonia and nitric acid.

In 1898, Sir William Crookes called attention to the fact that the world's natural resources of combined nitrogen would be exhausted within a relatively short period of time, and that methods of "fixing" the nitrogen in the air must be discovered. Due to the very slight chemical activity of free nitrogen the tremendous supply in the air is without value until compounds are made from it. At the beginning of World War II, the plants that had been constructed for the fixation of this nitrogen in the atmosphere had a total producing capacity of about 4,000,000 tons of nitrogen annually, and the actual production was probably about one half of that quantity. In addition, coal is still used to supply large amounts of ammonia, and Chile saltpeter supplies combined nitrogen for use in fertilizers and in making nitric acid, although industry is coming to depend less and less upon these sources and more and more upon the production of nitrogen compounds from the nitrogen of the air.

Free nitrogen is used in one of the processes for hardening steel. It is frequently used to replace air when an inert, non-oxidizing and non-reducing atmosphere is desirable. Electric lamps are generally filled with nitrogen or a mixture of nitrogen and argon. Mercury thermometers (especially those which are prepared for use at high temperatures) may contain nitrogen in the capillary space above the mercury. The introduction of nitrogen decreases the tendency of the metal to evaporate into this space and reduces the error in temperature reading that arises from this source.

A few compounds, besides ammonia, are made directly from the free element, one of the most important of these is calcium cyanamide, CaCN_2 , which is used as a fertilizer and also in the production of ammonia.

9. Nitrogen in the Soil

The rocks and soils of the earth's surface contain naturally very little combined nitrogen. Compounds of this element are, how-

ever, essential nutritive materials that plants must acquire from the soil. The mixtures sold and used as fertilizers for the enrichment of the soil contain compounds of one or more of the three elements, nitrogen, potassium, and phosphorus, and sometimes smaller amounts of compounds of other elements as well. The nitrogen in these mixtures is usually in the form of nitrates or ammonium salts KNO_3 , NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and $(\text{NH}_4)_3\text{PO}_4$. The manufacture of these compounds requires, in normal times, a large percentage of the world's production of ammonia and nitric acid.

In addition to the nitrogen added to the soil through the use of "chemical" fertilizers, there are various other agencies which contribute to the soil's fertility with respect to nitrogen, and there are other means by which the farmer can restore the nitrogen that is withdrawn by the removal of crops such as corn and wheat. Some nitrogen and oxygen combine under the influence of the electrical discharges that play across the sky during a thunderstorm. The compounds produced in this manner dissolve in the rain and eventually find their way into the soil, where they add at least something to the fertility over a long period of time. There is another natural method of nitrogen fixation, however, which is of much greater importance than lightning. Certain plants, called the *legumes*, have on their roots small nodules in which there are certain bacteria that have the unusual power of converting free nitrogen into compounds that plants can use. These bacteria probably first form proteins which are later changed into nitrates. The exact manner in which bacteria produce these compounds of nitrogen is unknown. With the aid of these bacteria the legumes are able to feed upon the nitrogen of the air. In addition to supplying their own needs, they "fix" more nitrogen, which remains in the soil to serve as food for other plants. The leguminous plants include alfalfa, clover, beans, and peas. The wise farmer

practices a system of crop rotation, in which each part of his cultivated land is planted in some leguminous crop at least once in four years. If the legume is "turned under," the soil is greatly enriched by the addition of all the nitrogen which the plants (and then coexisting bacteria) have been able to assimilate from the air. Crops turned beneath the soil in this manner are called "green" manures.

Some nitrogen finds its way back into the soil from the stubble of grain, from weeds, and from other plants that are allowed to decompose when they die. The farmer aids this process by adding various manures to the soil. These consist of nitrogenous organic materials, which in the process of decay are converted into ammonia, then into nitrites, and finally into nitrates. Bacterial action is important in all of these changes.

10 The Natural Nitrogen Cycle

Nitrogen appears to belong naturally only in the atmosphere of the earth. However, a relatively small amount of it is always found in the combined state on the earth's surface and in the soil. This small quantity of fixed nitrogen is not permanent but is ever undergoing changes which, taken together, make a cycle. Some nitrogen from the air is converted into compounds either by electrical discharges or by the action of the nitrifying bacteria that live upon the roots of leguminous plants. This nitrogen is then used by plants in synthesizing various complex substances which compose their own structures or which are stored in seeds, fruits, roots, blades, branches, or leaves. The product of the plant's assimilation of nitrogen is a protein of one kind or another. These proteins serve in part as foods for animals, which convert them during metabolism into other proteins, often of a higher order or more complex structure. Eventually many of them are converted into other substances and eliminated as waste products of the animal body. Other plant proteins,

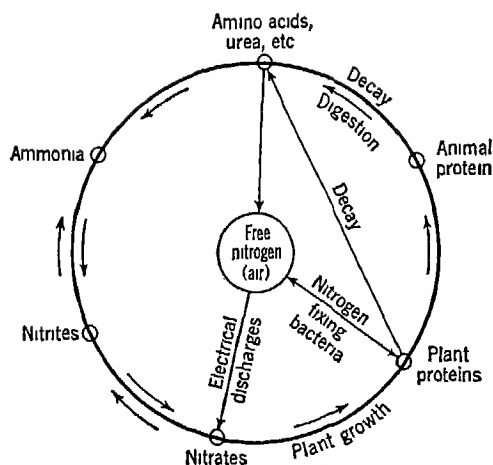


Figure 208 The Nitrogen Cycle

and animal proteins as well, finally undergo chemical changes involving decomposition and decay. Some may be destroyed by combustion. In these changes some of the nitrogen may escape into the free state, while the remainder is converted into ammonia, nitrites, and nitrates, in which forms a large part of the nitrogen may be returned to the soil. This cycle (Figure 208) is of extremely great importance to life on the earth. In all of these changes, soil bacteria are active agents. Certain bacteria convert nitrates into nitrites, free nitrogen, and ammonia, others act in the opposite direction to produce, first, nitrites, and then nitrates.

AMMONIA

11. Introduction, History

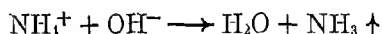
At one time, ammonia was prepared by heating the horns and hoofs of animals in the absence of air. The gas produced during the decomposition of these materials, which contain proteins, was dissolved in water to form a solution called "spirits of hartshorn." For some reason the name ammonia later came into general use. This name is probably derived from that of the Egyptian deity, Jupiter Ammon, near whose temple there was obtained, in early historical times, a mixture of salt and sodium carbonate. This

mixture was given the name of *sal ammoniacum*. Much later this name was applied to the salt, ammonium chloride, which is still called *sal ammoniac*. Pure ammonia was probably prepared for the first time about 1774, by Priestley, who heated sal ammoniac with slaked lime and collected the gas by displacing mercury. Similar experiments had been performed before, but these had attempted to collect the gas by displacing water and had resulted in failure because ammonia is very soluble in water. The name *ammonia* was given to the gas by Bergman (1782), and Berthollet (1785) determined the composition of the compound.

Throughout the following discussion careful distinction should be made between the term ammonia (NH_3) and the term *ammonium*, which refers to the NH_4^+ ion and which is present in solutions of ammonium hydroxide (NH_4OH) and the salts formed by this base (NH_4Cl , NH_4NO_3 , and $(\text{NH}_4)_2\text{SO}_4$).

12 Laboratory Method of Preparation

Laboratory samples of ammonia can be prepared from solutions of ammonium hydroxide. When the solution is warmed, ammonia escapes and, being lighter than air, can be collected by the upward displacement of air (Figure 209). The reaction is shown by the equation



(This reaction is not shown as reversible because of the escape of ammonia.) Instead

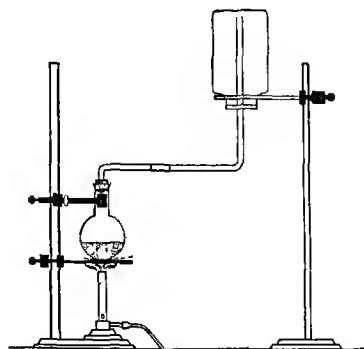
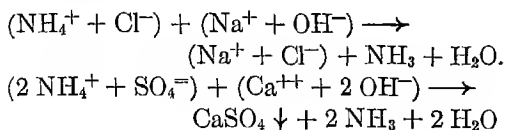


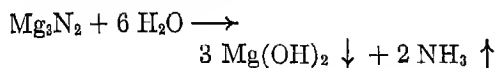
Figure 209 The Preparation of Ammonia and Its Collection by the Upward Displacement of Air

of using pure ammonium hydroxide solution, an ammonium salt may be treated with a base, such as sodium hydroxide or calcium hydroxide



The solid substances may be mixed to give the above reactions, if a trace of water is present, or the base may be added to a solution of the ammonium salt. These methods are not used, of course, for the manufacture of ammonia in large quantities, because ammonium salts, themselves, are produced from ammonia.

Ammonia is produced by the hydrolysis of magnesium nitride



Magnesium nitride is made by passing nitrogen over heated magnesium. This, also, is a laboratory method.

13 The Production of Ammonia from Coal

Coal contains an average nitrogen content of about one per cent. During destructive distillation a portion of this nitrogen (20 to 50 per cent) is converted into ammonia, and the remainder into free nitrogen. The coal gas that contains the ammonia is washed by passing it through "scrubbers" containing water. The ammonia dissolves, forming a solution of ammonium hydroxide and ammonium salts. This solution is called "ammoniacal liquor." It is treated with slaked lime to convert the ammonium salts into ammonium hydroxide, and the mixture is then heated with steam to drive off the ammonia. The ammonia, now in a more nearly pure state, is dissolved in water or in a solution of an acid, a large part of the ammonia produced from coal is dissolved in a solution of sulfuric acid and converted into ammonium sulfate, which is used chiefly as a fertilizer. About 20 pounds of ammonium

sulfate is produced from each ton of coal, the annual production in the United States is normally about 700,000 tons with at least as much more produced from synthetic ammonia.

14 The Haber Synthetic Ammonia Process

Of the several processes that have been proposed for the fixation of nitrogen the synthetic ammonia, or Haber, process is the most successful. It involves the direct synthesis of ammonia from nitrogen and hydrogen



During World War I, this process was operated for the first time on a large scale in Germany to supplement the production of ammonia from coal. Ammonia was used to produce nitric acid, which was required for the manufacture of explosives. Since sodium nitrate could not be imported from South America, the military forces of Germany could not have waged war for four years without the Haber process to supply

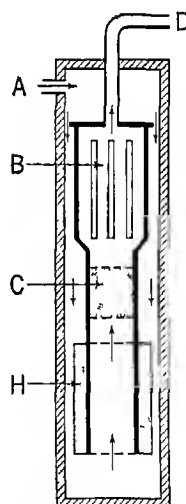


Figure 210 The Reaction Chamber of the Haber Synthetic Ammonia Process

The mixture of nitrogen and hydrogen enters at A, passes down around the catalytic chamber and finally over the catalyst at C. The gaseous mixture is heated, before passing over the catalyst, in H, where heat is supplied by the flow of an electric current through resistance wire. After the reaction in C, the gases flow out through the cooling chamber B and into absorbing towers through D.

their needs. Before that war was ended, the same process, or modifications of it, was used in other countries, and at the outbreak of World War II it was the principal source of ammonia and, indirectly, of nitric acid in all the countries engaged in the conflict.

The reaction upon which the process is based is reversible and exothermic. According to Le Châtelier's principle (page 429) an increase in the temperature should favor the reverse reaction and thus reduce the percentage of nitrogen that is converted into ammonia. The effect of an increase in temperature is shown in Table 26, columns 1 and 2. These data show that it is possible to convert a fairly high percentage of nitrogen into ammonia at 200°. At that temperature, however, the speed of the reaction is so slow that it is not commercially of any value. When the temperature is increased, the speed of the reaction is also increased, but the percentage of ammonia in the equilibrium mixture (Table 26, column 2) is so small, above 300°, that the reaction cannot be used economically to make ammonia. The only possible solution to a problem of this kind is a catalyst that will accelerate the reaction at a temperature for which the equilibrium mixture contains a satisfactory percentage of ammonia.

One other factor can also be controlled in such a way that the percentage of ammonia is increased for a given temperature. This is the pressure of the gases in the reacting mixture. From the equation for the reaction it is evident that one volume of nitrogen reacts with three volumes of hydrogen to form two volumes of ammonia. The reaction is favored, therefore, by high pressure. The effect of pressure is shown by the data in Table 26, columns 2-5.

The details of the synthetic ammonia process are briefly summarized below.

(1) *Pressure* Haber first used a pressure of about 200 atmospheres. Carbon-free chromium steel was found to be necessary for the bombs or vessels in which the reaction was carried out, because hydrogen diffused rapidly through walls

made of ordinary steels. Higher pressures have been used. In some plants pressures up to 1000 atmospheres are used. At 200° and 1000 atmospheres, the percentage of ammonia in the equilibrium mixture is about 98.

(2) *Temperature* Even with the aid of a suitable catalyst, the speed of the reaction is too slow, unless the temperature is maintained at 400°-600°.

TABLE 26

Effect of Temperature and Pressure upon the Production of Synthetic Ammonia

Temperature Degrees C	Percentage of Ammonia in the Equilibrium Mixture			
	1 at- mos- phere	100 at- mospheres	200 at- mospheres	250 at- mospheres
200°	15.3		86.0	
300°	2.2			
500°	0.13	10.2	17.6	20.0
600°	0.05	4.5	8.2	9.5
700°	0.02	2.0	4.0	5.0
800°	0.01	1.1	2.2	2.8
900°		0.8	1.2	1.8
1000°	0.004	0.4	0.9	1.2

(3) *Catalysts* The industry is always seeking a catalyst which will accelerate the speed of the reaction so that it may be operated at a lower temperature, at which the percentage of ammonia in the equilibrium mixture is higher. Among the catalytic substances which have been used are osmium, uranium, a mixture of iron and molybdenum, and a mixture of iron oxide and potassium aluminate (potassium oxide and aluminum oxide).

(4) *Materials* Nitrogen is obtained from liquid air, and hydrogen from water gas or from similar gases produced by the action of steam upon different hydrogen compounds of carbon. Both elements can be obtained simultaneously by blowing a mixture of steam and air over hot coke; steam supplies the hydrogen and air the nitrogen, while the coke removes the oxygen of the air and reduces water, forming carbon monoxide.

The carbon monoxide must be removed, this is accomplished by the method described for the preparation of hydrogen from water gas (page 111). Other sources of hydrogen (page 111) may also be used. The gases used in the reaction must not contain substances that poison (page 421) the catalyst. Their purification, and especially the



Courtesy of the American Cyanamide Company

Figure 211 Fixation Ovens in Which Electrically Heated Calcium Carbide and Nitrogen React to Form Calcium Cyanamide

purification of hydrogen, is sometimes the most difficult problem of the industry, since very large quantities must be made available.

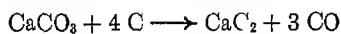
(5) The essential parts of the equipment of a plant for the production of synthetic ammonia are shown in Figure 210

15. The Cyanamide Process

Ammonia can also be produced from calcium cyanamide, CaCN_2 , which is made from coke, limestone, and free nitrogen

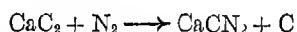
The steps involved in this process employ inexpensive raw materials but require large amounts of energy. The process may be described and explained by the following reactions

(1) Limestone is heated with coke in an electric furnace. The coke reduces the limestone and forms calcium carbide (page 311)

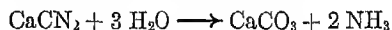


(2) Calcium carbide is heated to a temperature of about 1000° and nitrogen (obtained from liquid

air) is passed over it. This produces calcium cyanamide (CaCN_2 or CaNCN)



(3) Calcium cyanamide is then treated in autoclaves with steam under pressure



During World War I, more than half of the nitrogen converted into compounds was fixed by the cyanamide process. Some thirty plants for the operation of this process were constructed, or at least construction was begun, in this country during 1917-18, the best known of these was the government's plant at Muscle Shoals, Alabama, that cost \$80,000,000 and was designed to fix 40,000 tons of nitrogen annually. Under normal conditions, however, the cyanamide process for making ammonia cannot compete with either the Haber process or production from coal.

In 1917, the world's production of syn-

thetic ammonia by the cyanamide process amounted to about 200,000 tons (calculated as fixed nitrogen). In the same year about 100,000 tons of nitrogen was converted into ammonia by the Haber process. In 1936 the fixation of nitrogen by the latter process was more than 1,000,000 tons while the production by the cyanamide process had increased to about 270,000 tons.

The cyanamide, itself, may be used as a fertilizer, because it slowly reacts with water to produce ammonia which, in the soil, is eventually changed, at least in part, into nitrate. When so used, it is sometimes called "lime nitrogen." It is also used in the manufacture of certain compounds of nitrogen, such as the cyanides. Although not a direct competitor in the production of ammonia, the cyanamide process is used to fix about 12 to 15 per cent of all the nitrogen that is converted each year into useful compounds. The post-war producing capacity of the United States is estimated as 100,000 tons per annum.

16. Physical Properties of Ammonia

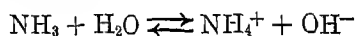
Ammonia is a colorless gas. It is readily detected by its sharp, irritating, and suffocating odor. If pure ammonia is breathed, it is very poisonous in its effects and may cause death in a few minutes, but when greatly diluted with air, it appears to have no serious effects. Its density is a little more than half that of air, under standard conditions, one liter weighs 0.771 g. It can be collected, therefore, by the upward displacement of air. It cannot be collected over water because it is very soluble, one volume of water at 20° dissolves about 700 volumes of ammonia under one atmosphere of pressure. Its critical temperature is 132.4°, and its critical pressure is 111.5 atmospheres, therefore, it is easily liquefied. The liquid boils at -33.4° and freezes at -77.7°. Its heat of vaporization — 327 calories per gram — is greater than that of any liquid except water. This, together with the ease with which it can be liquefied, makes ammonia a

suitable substance to use in refrigerators and in the manufacture of ice. The concentrated aqueous solution (aqua ammonia) contains about 28 per cent of ammonia at ordinary temperatures and weighs about 0.9 g per cc. Liquid ammonia resembles water to some extent in its action as a solvent, it has a high dielectric constant and serves, therefore, as a good ionizing medium for electrolytes.

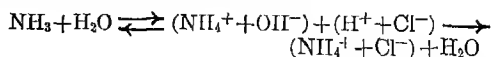
17. Chemical Properties of Ammonia

In some of its chemical properties ammonia also resembles water, but the two compounds differ greatly in certain other respects. Ammonia, for example, burns readily in pure oxygen and reduces the oxides of some of the metals. Its chemical behavior is best described by specific reactions.

(1) Ammonia reacts with the water in which it dissolves to form small concentrations of ammonium and hydroxyl ions. In this reaction ammonia acts as a base and water as an acid.

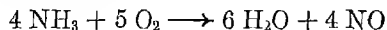


The solution is referred to, usually, as a solution of the weak base, ammonium hydroxide (page 438). The reaction is reversible, and if the solution is heated, ammonia escapes, and the reaction to the left eventually is completed. If an acid is added to the solution, the hydroxyl ions are converted into molecules of water, this causes the equilibrium to shift toward the right, and a solution containing the ions of an ammonium salt of the acid is produced.



When ammonia and hydrogen chloride are mixed as gases, ammonium chloride is produced in the form of a white cloud, which can serve as an effective smoke screen. It is very likely that in an aqueous solution of ammonia some ammonium and hydroxyl ions combine by means of hydrogen bonds to form molecules of NH_4OH .

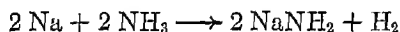
(2) Ammonia burns readily in pure oxygen to form water and nitrogen. In air the combustion is more difficult to initiate and maintain. Mixed with about ten times its volume of air and passed over a platinum gauze heated to 600° , ammonia is oxidized to form nitric oxide and water:



This reaction is the basis of an important method of converting ammonia into nitric acid (page 482).

(3) Ammonia acts as a reducing agent and, as such, it reduces the oxides of certain metals to the free metals. Its reduction of hot cupric oxide has been mentioned (page 466) as a method of producing free nitrogen.

(4) The reaction of ammonia with the alkali metals, sodium and potassium, reminds us of the reaction of water with the same metals:

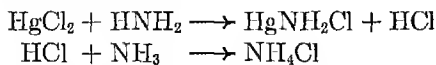


The compound NaNH_2 is sodium amide or *sodamide*, and the $-\text{NH}_2$ group is the *amido* or *amino* radical. Sodamide is a substance of considerable commercial importance.

Other metals displace all the atoms of hydrogen from the molecule of ammonia and form nitrides of the metals:



(5) Ammonia also reacts with some salts in the same manner that water does when these salts hydrolyze:



(6) Ammonia reacts with some salts to form *ammoniates* in the same manner that water forms hydrates. With calcium chloride, for example, ammonia forms $\text{CaCl}_2 \cdot 8 \text{NH}_3$.

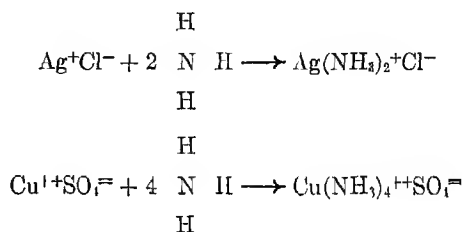
(7) With mercury ammonia forms the amalgam, NH_4Hg , which decomposes to form hydrogen:



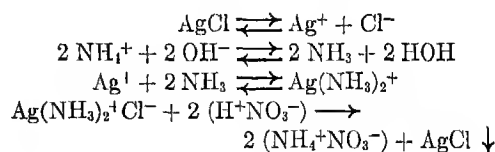
18 Complex Ions Containing Ammonia

Many metallic ions combine with ammonia to form complex ions sometimes called *ammines*. These substances correspond to the hydrated ions produced by metallic ions and water, e.g., $\text{Al}(\text{H}_2\text{O})_6^{+++}$, (page 455).

They are thought to be produced when the nitrogen atom of the ammonia molecule shares its unused pair of electrons with the metallic ion (page 183):



These complex ions are only slightly dissociated ($\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2 \text{NH}_3$) in solution. Hence, the concentration of the silver ion is easily reduced to a very small value by adding ammonia to a suspension of silver chloride in water. It becomes so small that the solubility product of silver chloride is not exceeded, and this substance then dissolves completely if enough ammonia is added. The reaction is reversible; if an acid is added, it reacts with ammonia, the silver ion is released and, in the presence of chloride ion, reprecipitates as silver chloride:



19. Uses of Ammonia

Ammonia is used to manufacture other compounds of nitrogen. Of these, nitric acid is most important, but large quantities are also converted into ammonium sulfate, ammonium nitrate, ammonium carbonate, ammonium chloride, and other ammonium salts. It is also used in the liquid state in refrigeration and in the manufacture of ice (Figure 212). As "aqua ammonia" it is used as a cleansing agent and water softener.

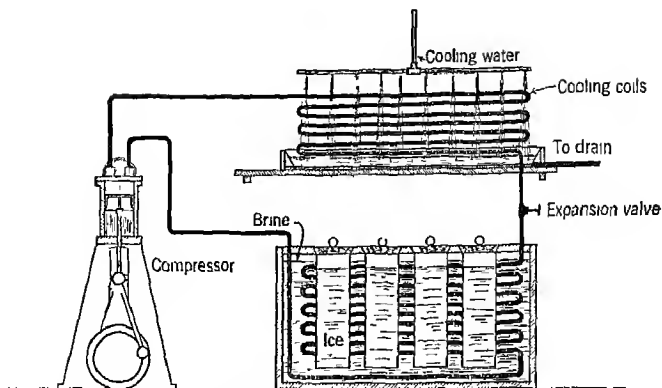


Figure 212 The Production of Ice by Means of Ammonia

The cooling that results in the formation of ice is brought about by allowing the compressed, liquefied ammonia to change into the gaseous state in the coils that surround the tanks in which the ice is formed. The change to the gaseous state occurs when the liquid ammonia is allowed to evaporate after passing through the expansion valve into the coils, where the pressure is lower. The gas is then returned to the compressor and there is liquefied again.

The use of ammonia in the Solvay process for producing soda has already been discussed (page 382).

Liquid ammonia, if allowed to boil rapidly

under reduced pressure, can be used to produce temperatures as low as -50° . It is used in this way in the quick-freezing process of preserving foods.

Some of the other substances used in refrigerating units, especially in domestic electric refrigerators, are sulfur dioxide, methyl chloride, CH_3Cl , and dichlorodifluoromethane, CCl_2F_2 .

20 Ammonium Compounds

A solution of ammonia in water contains ammonium and hydroxyl ions and therefore acts as a weak base; it neutralizes acids to form ammonium salts, in which the NH_4^+ radical, or ion, acts in the same manner as a univalent metallic ion, such as Na^+ or K^+ . When any ammonium salt is treated with a hydroxide, such as NaOH , KOH , or $\text{Ca}(\text{OH})_2$, the ammonium ion of the salt reacts with the hydroxyl ion of the hydroxide to form ammonia and water. Since a portion of the ammonia escapes—and all of it in time, especially if the mixture is heated—it can be detected by means of a moist strip of red litmus paper, by its odor, or by its reaction with hydrogen chloride, with which it forms a white cloud of ammonium chloride. The hydrogen chloride may be produced by allowing some of it to vaporize from a drop

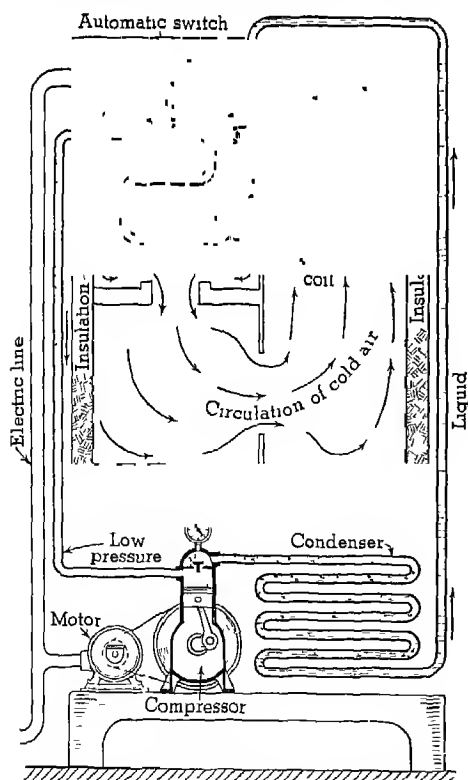
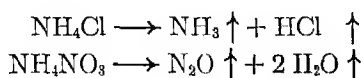


Figure 213 An Electric Refrigerator

of concentrated hydrochloric acid that is suspended on the end of a stirring rod held in the fumes of the escaping ammonia. This procedure is used as a test for ammonium compounds.

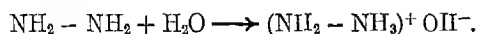
Ammonium salts differ from the corresponding compounds of sodium and potassium in two respects: (1) they are hydrolyzed to a greater extent, because ammonium ion reacts with the hydroxyl ion of water, while sodium and potassium ions do not, and (2) ammonium salts are decomposed easily by heat.



Ammonium chloride is used in medicine, as a flux in soldering, and in manufacturing dry cells. Ammonium sulfate is an important fertilizer (page 471). Ammonium nitrate is an explosive. Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, mixed with alcohol and aromatic oils, is used as "smelling salts." Ammonium carbamate, $\text{NH}_4\text{CO}_2\text{NH}_2$, is produced by a reaction between carbon dioxide and ammonia. It is used as a fertilizer and in the manufacture of certain plastics.

21. Other Compounds of Nitrogen and Hydrogen

Hydrazine (N_2H_4) is a colorless liquid. The molecule may be regarded as having the structure $\text{NH}_2 - \text{NH}_2$. Hydrazine reacts with water to form a base:

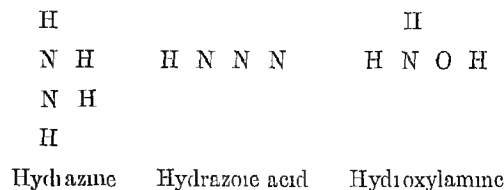


The $(\text{NH}_2 - \text{NH}_3)^+$ ion may be regarded as a derivative of the ammonium ion in which one hydrogen atom of the NH_4 group is replaced by the NH_2 radical. This base neutralizes acids to form salts. Hydrazine hydrochloride, for example, is $\text{NH}_2 - \text{NH}_3\text{Cl}$.

Hydrazoic or *hydronitric acid* (HN_3) contains the univalent N_3^- ion, which resembles somewhat the univalent chloride ion. The acid neutralizes ammonium hydroxide to form the salt NH_4N_3 . The acid and its salts are very unstable and usually decompose explosively.

Hydroxylamine, NH_2OH , or NH_2OH , reacts with

water to form $(\text{NH}_2 - \text{OH})^+$ and OH^- ions and forms salts, such as hydroxylamine hydrochloride, NH_2OCl , or $(\text{NH}_2 - \text{OH})^+ \text{Cl}^-$.



Review Exercises

- Why was nitrogen first regarded as "completely phlogisticated" air?
- Why should nitrogen, which composes almost 80 per cent of the air, have remained undiscovered until about 1800?
- How does nitrogen that is prepared from air differ from nitrogen prepared from ammonium nitrite?
- A steel cylinder contains 100 liters of nitrogen at 20°C and under a pressure of 100 atmospheres. What weight of nitrogen does the cylinder contain?
- What is the maximum weight of nitrogen that can be obtained by passing 24 (standard) liters of ammonia over cupric oxide?
- Describe the structures of the atom and the molecule of nitrogen.
- How is the chemical inactivity of molecular nitrogen explained? How does "active" nitrogen differ from ordinary nitrogen?
- Describe the chemical changes involved in the decomposition and decay of plant and animal proteins.
- What are the two principal natural sources of combined nitrogen?
- In what natural ways is the soil enriched in nitrogen content?
- Summarize the three principal methods of producing ammonia on an industrial scale. Compare these processes, showing what advantages, if any, each has over the other two.
- State the conditions that favor the reaction of the Haber process, and explain how a change in each condition affects the reaction.
- Illustrate each of the important chemical properties of ammonia by an equation. In what chemical respects is ammonia somewhat like water?

- 14 How does the nitrogen atom combine with three atoms of hydrogen in forming the molecule of ammonia?
- 15 Describe the cycle of nitrogen and its compounds in nature
- 16 Why do the hydroxides of some metals dissolve in a solution of ammonia?
- 17 Describe the reactions employed in the cyanamide process for the production of ammonia. Why is this process not used as extensively as the Haber process?
- 18 What ions and molecules are present in an aqueous solution of ammonia?
- 19 What volume (standard) of ammonia can be produced from 100 g of calcium cyanamide?
- 20 What is sodamide and how is it produced?
- 21 Explain the use of ammonia in a refrigerating unit
- 22 What (standard) volume of ammonia is required to neutralize one liter of 6 N sulfuric acid?
- 23 A solution of ammonia (ammonium hydroxide) contains 28 per cent of ammonia and has a specific gravity of 0.9. What volume of this solution is required to produce 62 g of ammonium nitrate?
- 24 Why is sulfuric acid, which is a good drying agent, not used to dry ammonia?
- 25 Give an example of a reaction in which the ammonium ion acts as an acid
- 26 Assuming that coal contains one per cent of nitrogen, thirty per cent of which can be recovered as ammonia, what weight of coal is required to produce 100,000 tons of ammonium sulfate?
- 27 If 100 g of ammonium chloride is treated with sodium hydroxide and the ammonia is recovered completely and converted into ammonium nitrate, what weight of nitric acid is required?
- 28 If the ammonia is completely oxidized, in the presence of platinum, to form nitric oxide, NO , what volume of the latter, under standard conditions, can be produced from one liter of liquid ammonia, which has a density 0.62 g per milliliter?
- 29 What (standard) volume of air must be used to produce the liquid ammonia required to fill a cylinder holding 100 liters? Assume that all the nitrogen of the air is converted into ammonia by the Haber process
- 30 What (standard) volume of ammonia can be produced from 10 g of ammonium chloride?
- 31 Write equations for reactions that occur when
 - (a) Ammonia is converted into nitric oxide
 - (b) Ammonium nitrate is heated
 - (c) Calcium cyanamide reacts with steam
 - (d) Magnesium nitride hydrolyzes
 - (e) Calcium hydroxide reacts with ammonium sulfate
 - (f) Silver chloride dissolves in a solution of ammonium hydroxide
 - (g) Calcium carbide reacts with nitrogen
 - (h) Sodium reacts with ammonia
 - (i) Mercuric chloride reacts with ammonia
 - (j) Hydroxylamine reacts with hydrochloric acid
- 32 State the procedure that you would use to convert
 - (a) Ammonium chloride into ammonium nitrate
 - (b) Ammonium ion into ammonia
 - (c) Ammonia into ammonium ion
 - (d) Ammonia into free nitrogen
 - (e) Ammonium chloride into free nitrogen.

References for Further Reading

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- Slosson, E. E., *Creative Chemistry*, chaps. III-VII.
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- Nitrogen Industry. *Chem. and Met. Eng.*, **43**, 282 (1936), *Ind. and Eng. Chem.*, *News Edition*, **17**, 86 (1939), **18**, 759 (1940), **23**, 243 (1945).

OTHER COMPOUNDS OF NITROGEN

The secret of chemistry is rather possible than impossible. Its mysteries are only revealed by dint of hard work and tenacity. But what a triumph when man is able to raise a corner of the veil which covers nature.

RIIAZES

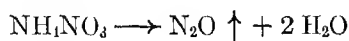
1. Introduction

There are many compounds of nitrogen and, of these, a large number belongs to organic chemistry. In this chapter, however, we shall confine our study to the oxides, the acids that contain oxygen, and to the salts of these acids — the nitrites and the nitrates. At the close of the chapter we shall also discuss a few of the compounds containing the cyanide, $-\text{CN}$, group.

OXIDES AND OXYGEN ACIDS OF NITROGEN

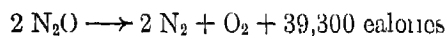
2 Nitrous Oxide

This oxide of nitrogen is a colorless gas at ordinary temperatures. It can be prepared by carefully heating ammonium nitrate.



If the heating is very vigorous, ammonium nitrate may decompose explosively. The gas is usually collected over warm water.

Nitrous oxide is an endothermic compound.



It is, consequently, unstable and acts as a vigorous oxidizing agent. A glowing splint will burst into flame in an atmosphere of this gas almost as readily as in pure oxygen. This oxide may be regarded as the anhydride of the unstable and explosive *hyponitrous acid*, $\text{H}_2\text{N}_2\text{O}_2$.

Sir Humphry Davy discovered the peculiar, exhilarating and intoxicating effects of nitrous oxide. It is called *laughing gas*, because of the hysterical laughter that it causes, although sometimes the hysteria may be manifested by weeping instead of by laughter. Dentists and surgeons use it.

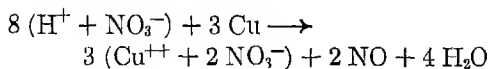
TABLE 27
Oxides of Nitrogen

Name	Formula	Physical Properties
Nitrous oxide	N_2O	Colorless gas, boiling point -90°
Nitric oxide	NO	Colorless gas, boiling point -154°
Nitrogen trioxide	N_2O_3	Blue liquid, boiling point 3.5°
Nitrogen dioxide	NO_2	Red-brown gas, at 21.3° and lower, a colorless gas N_2O_4 , or a light yellow liquid
Nitrogen pentoxide	N_2O_5	White solid, melting point 30°

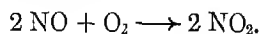
in minor surgical cases as an anesthetic that is pleasant, quick in its action, and without harmful after-effects. When so used it must be mixed with oxygen, which it cannot replace in meeting the body's requirement, although it is a vigorous oxidizing agent. It is not oxidized by oxygen, under ordinary conditions, to any of the higher oxides, such as NO .

3 Nitric Oxide

Small quantities of this oxide are produced from the oxygen and nitrogen of the air during thunderstorms, a natural nitrogen-fixation process. It was first prepared by Henry Cavendish, who subjected a mixture of the two elements to an electrical discharge, which acted in the same manner as lightning flashes during a storm. It has also been made — on an industrial scale — by a similar reaction in which a mixture of oxygen and nitrogen is passed through an electric arc, this reaction is the basis of the *arc process*, which was once used to a limited extent to manufacture nitric acid from air. It is also produced by the oxidation of ammonia in air and in the presence of a platinum catalyst (page 482); this reaction is the first step in the production of nitric acid from ammonia, a process to which we shall return a little later. In the laboratory, nitric oxide can be prepared most easily by allowing dilute (about 6 N) nitric acid to act upon copper.



Nitric oxide is a colorless gas and is only slightly soluble in water. Its most important chemical property is its reaction with oxygen to form nitrogen dioxide.



It acts, therefore, as a reducing agent. It may also act as an oxidizing agent, but it is much more stable than nitrous oxide. It extinguishes a burning splint of wood and

also burning phosphorus, unless the latter is burning very vigorously.

4. Nitrogen Trioxide

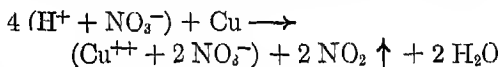
This oxide is the anhydride of nitrous acid (HNO_2). It can be prepared by treating a salt of nitrous acid with sulfuric acid. The acid is liberated and decomposes, under ordinary conditions, into water and a mixture of two gases, NO_2 and NO , which escape as the mixture is warmed. When a mixture of these two oxides is cooled to -21° , a blue liquid is produced, and this has a composition corresponding to the formula N_2O_3 . At higher temperatures, nitrogen trioxide and its decomposition products, NO and NO_2 , are probably in equilibrium.



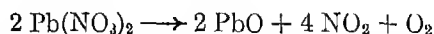
At room temperature this equilibrium is probably displaced almost completely toward the right.

5. Nitrogen Dioxide

This oxide can be prepared by allowing concentrated nitric acid to act upon copper.



It is also prepared by heating the nitrate of a heavy metal, such as lead.



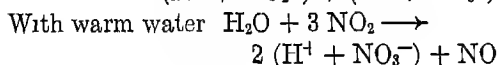
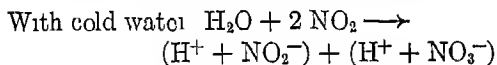
Nitrogen dioxide is produced on an industrial scale by allowing nitric oxide to react with the oxygen of the air.

The comparison of the action of concentrated nitric acid upon copper and of the dilute acid upon the same metal is interesting. There are several possible explanations of why NO is liberated in one case and NO_2 in the other. If NO is formed in both cases (and this appears to be the likely course of the reaction), it is oxidized to NO_2 by the excess of concentrated acid. If NO_2 is formed in the case of the dilute acid, it may react with the excess of water to produce nitric acid and NO . $3 \text{NO}_2 + \text{H}_2\text{O} \longrightarrow 2 \text{HNO}_3 + \text{NO}$. Just what does happen in either case is not

entirely established, but these suggestions are plausible

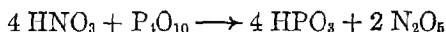
At temperatures above 600° , nitrogen dioxide dissociates into nitric oxide and oxygen. At about 150° , the density of the gas corresponds to the formula NO_2 . At 21° and lower, the formula appears to be N_2O_4 . Between 21° and 150° , the gas appears to consist of a mixture of NO_2 and N_2O_4 . The oxide, N_2O_4 , is a *polymer* of NO_2 . This name is applied, generally, to compounds whose molecular weights are multiples of the molecular weight of the simplest form of the compound. The oxide, N_2O_4 , is called nitrogen tetroxide.

Nitrogen dioxide is very poisonous. It acts as an oxidizing agent, but supports combustion only with difficulty and at fairly high temperatures. It is also a reducing agent, since it can be converted into nitric acid and the nitrates. The most important property of NO_2 is its reaction with water.



6. Nitrogen Pentoxide

This oxide is the anhydride of nitric acid. It is a white crystalline solid. It may be produced by dehydrating nitric acid by means of phosphorus pentoxide.



7. Nitrous Acid and the Nitrites

Nitrous acid has never been prepared in the pure state. We assume, however, that it is formed whenever a mixture of NO and NO_2 is passed into water (page 480) or, along with HNO_3 , when NO_2 is passed alone into cold water. The solution thus produced appears to contain such an acid, because when it is neutralized with NaOH and the solution is evaporated, crystals of sodium nitrite (NaNO_2) are obtained. Whenever an acid is added to a nitrite, we may assume

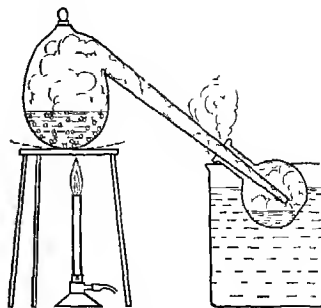
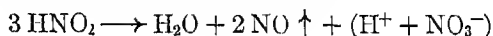


Figure 214 The Preparation of Nitric Acid in the Laboratory

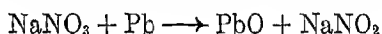
Sodium nitrate and sulfuric acid are heated in the retort. Pure nitric acid is condensed in the neck of the retort.

that the hypothetical acid, HNO_2 , first forms and immediately decomposes.



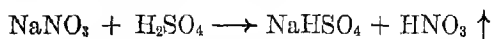
Sodium and potassium nitrites are the most important salts of this acid. They are used as laboratory reagents and in the manufacture of certain organic chemicals and dyes.

Sodium nitrite is prepared by passing a mixture of NO and NO_2 into a solution of NaOH , by heating sodium nitrate at a temperature above the melting point, and by heating sodium nitrate with metallic lead.



8. The Production of Nitric Acid from Sodium Nitrate

The most convenient method of producing nitric acid in the laboratory involves the distillation of a mixture of sodium nitrate and concentrated sulfuric acid.



This reaction is similar to the one used to produce hydrochloric acid from sodium chloride. In the manufacture of nitric acid, however, the second step, in which sodium bisulfate reacts with more sodium nitrate, is not carried out because it requires a fairly high temperature at which nitric acid decomposes. Until quite recently, almost all nitric acid was made from sodium nitrate,

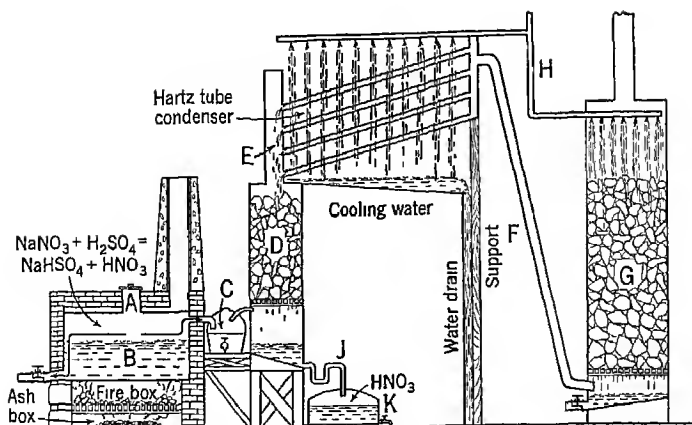


Figure 215 Nitric Acid Plant

The charge of sodium nitrate and sulfuric acid is added through A. B is the retort, C is a trap to catch the overflow from the retort, D is a tower containing quartz chips over which the nitric acid that is condensed in the tube condensers flows, in D the rising fumes of hot nitric acid remove the oxides of nitrogen that are present in the condensed acid. The lost traces of HNO_3 are absorbed in the tower G by water which flows over the quartz chips with which the tower is filled.

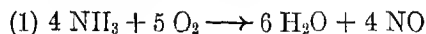
but this process has now been replaced very largely by production from ammonia. In fact, sodium nitrate supplies only about 8 per cent of the total world's production of about 3,000,000 tons of combined nitrogen. The essential parts of a nitric acid plant using this reaction are shown in Figure 215. The nitric acid is distilled from an iron retort under reduced pressure in order to avoid decomposition. The acid is condensed in tubes made of glass, silica, or Durrone, which resist the action of the acid. The solution of the acid obtained in this manner may be concentrated by mixing it with concentrated sulfuric acid and redistilling. Nitrogen dioxide may be removed by bubbling air through the acid. The decomposition of the acid is accelerated by light, hence, concentrated nitric acid which is stored in colorless bottles and exposed to the light usually has a brown color due to the presence of NO_2 .

9 Production of Nitric Acid from Ammonia

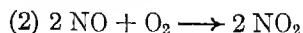
This is sometimes called the *Ostwald* process of producing nitric acid. The process depends upon the oxidation of ammonia by air in the presence of a catalyst, usually platinum. The air is filtered and forced by a pump into the reaction chamber, where it is mixed with ammonia in the ratio, by vol-

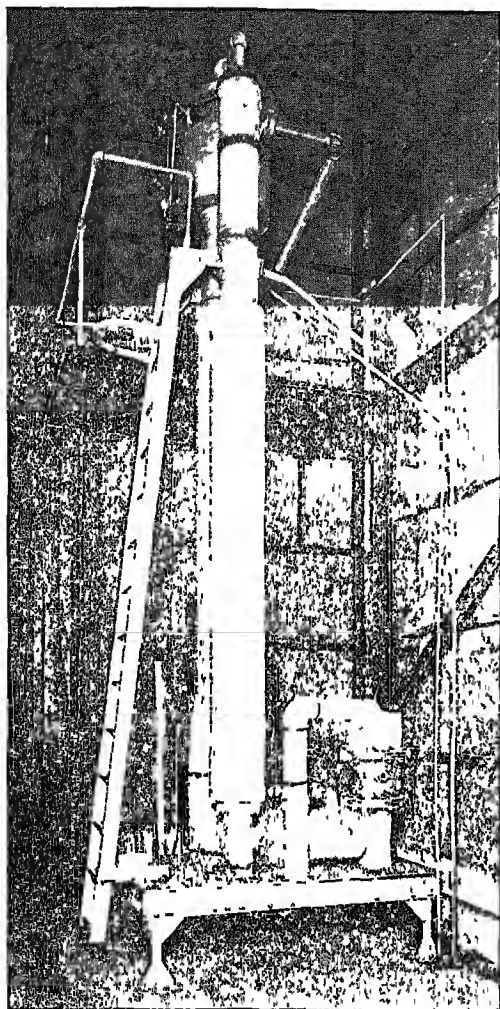
ume, of about ten to one. The mixture of gases then passes over the catalyst, which is a platinum gauze. This gauze is heated to about 700° in the beginning by means of an electric current, but the reaction, when it is once started, liberates sufficient heat to maintain the required temperature. In fact, care must be taken to prevent the temperature from becoming too high, because the reaction is exothermic and therefore is not favored by high temperature.

The following reaction occurs in the chamber containing the catalyst



The products of oxidation next pass through a chamber where they come into contact with pipes carrying air on its way to the pump and the chamber containing the catalyst. Here the gases—containing NO —are cooled, and the air in the pipes is heated before it comes into contact with the catalyst. The mixture containing nitric oxide is cooled still further by passing it through another chamber containing pipes through which cold water is flowing. The cooled nitric oxide then reacts with more oxygen to form nitrogen dioxide

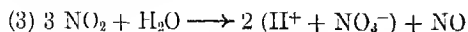




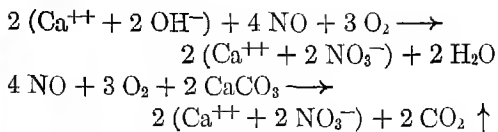
Courtesy of Baugh and Sons Co., and the Chemical Construction Corp.

Figure 216 An Oxidation Unit for the Conversion of Ammonia into Nitric Acid

The nitrogen dioxide then passes into an absorption tower, where it reacts with warm water as follows



The nitric oxide resulting from this reaction is returned to the process (2) and again converted into NO_2 . Sometimes this nitric oxide is mixed with air and converted directly into nitrates by passing it into a solution of a base, such as NaOH or $\text{Ca}(\text{OH})_2$ (in suspension), or by allowing it to react upon a mixture of limestone and water



The solution of nitric acid produced in this process contains about 60 per cent of HNO_3 . It is further concentrated by being distilled from a mixture with sulfuric acid. Coupled with the Haber process for producing ammonia, the Ostwald process has solved the problem of obtaining nitric acid from the nitrogen of the atmosphere. Almost all the nitric acid used in the United States is produced in this way.

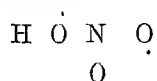
10. The Physical Properties of Nitric Acid.

When nitric acid is pure, it is a colorless liquid, which has a density of 1.50 g per cc, boils at 86° , and freezes at -42° . The constant boiling aqueous solution (b.p. 120.5°) contains 68 per cent of HNO_3 and has a density of 1.4 g per cc. This is the ordinary concentrated nitric acid used in the laboratory and in the industries. This solution dissolves the oxides of nitrogen, especially NO_2 , and forms a brown solution, called *fuming nitric acid*. This solution fumes in the air, is less stable, and reacts more vigorously as an oxidizing agent than the ordinary concentrated solution. It contains about 96 per cent of HNO_3 .

11 The Chemical Properties of Nitric Acid

Chemically, nitric acid acts as a strong acid and a vigorous oxidizing agent. As an acid, its degree of ionization is about the same as that of hydrochloric acid, it is, therefore, one of the strongest acids. As an oxidizing agent it reacts with many substances: sulfur is oxidized by it to sulfur dioxide or to sulfuric acid, carbon reacts with it to form carbon dioxide, and a piece of ignited charcoal continues to burn when placed in the concentrated acid, phosphorus is converted into phosphoric acid, H_3PO_4 or HPO_3 , and iodine is oxidized to iodic acid (page 372). The general behavior of the pure acid, rather than of its aqueous solution with

which we are more familiar, indicates that its structural formula is

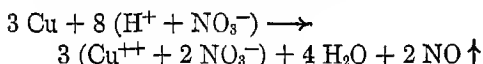


Some of the most important reactions of the compound are described in the sections that follow

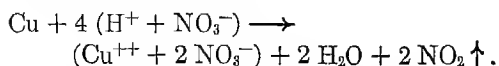
12. Action upon Metals

Nitric acid reacts with most metals, platinum, gold, and a few of the rarer metals are exceptions. In this respect it differs from hydrochloric acid, which reacts only with the metals above hydrogen in the electrochemical series. Nitric acid reacts with the less active metals because of its properties as an oxidizing agent, whereas in solutions of hydrochloric acid the metals can only displace hydrogen.

When moderately dilute — let us say 6 N — nitric acid reacts with copper, the nitrogen is reduced from a valence number of 5 to one of 2, and nitric oxide is formed

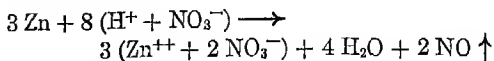


If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitric oxide, nitric oxide, however, may be formed first, but if it is formed it is later oxidized to the dioxide by the excess of acid. We cannot be certain that this is the exact course of the reaction, it is possible that the dioxide is formed directly. The ultimate reaction of copper and concentrated nitric acid is represented by the equation

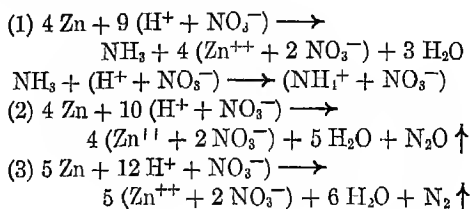


It is often impossible to predict the final valence number of the nitrogen when the acid acts upon the more active metals, such as zinc or aluminum. The nitrogen may appear among the products of the reaction as NO_2 , NO , N_2O , N_2 , NH_3 , or NH_4NO_3 . If nitrogen trioxide should be formed, it decomposes into NO and NO_2 . In general, the greater changes in valence occur when dilute

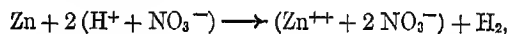
nitric acid and an active reducing agent react. With more concentrated acid and a less vigorous reducing agent, the product is more likely to be NO or even NO_2 . With zinc, for example, the usual reaction is



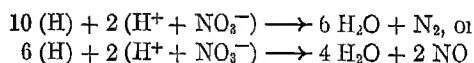
If the acid is dilute, any or all of the following reactions with zinc may occur



The reaction of nitric acid upon metals above hydrogen in the electrochemical series usually does not result in the liberation of hydrogen. Some hydrogen may be set free during the course of the reaction,



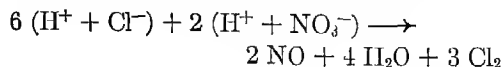
but unless the nitric acid is very dilute, this hydrogen is oxidized to water before it has an opportunity to escape. This is especially likely to occur since the hydrogen is liberated in the atomic form



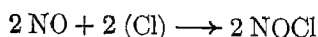
Under ordinary conditions, nitric oxide is usually produced

13. Action upon Hydrochloric Acid

Nitric acid oxidizes hydrochloric acid to form free chlorine, water, and an oxide of nitrogen, usually NO , according to the generally accepted explanation, the reaction is



The chlorine is liberated in the atomic form and reacts very vigorously upon metals and other substances. Some of the chlorine reacts with nitric oxide to form *nitrosyl chloride* (NOCl)



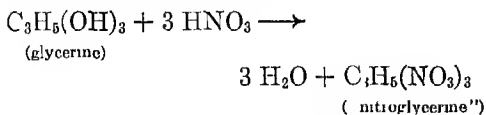
The formation of this compound casts some doubt upon the validity of the equation shown above to explain the reaction of the two acids

A mixture of one part of nitric acid and three parts of hydrochloric is often called *aqua regia* (royal water). This name was first used by the alchemists, because the mixture of acids dissolves gold, platinum, and other "noble" metals, which are not affected by either acid alone. The effect of *aqua regia* upon these metals probably is the result of the action of atomic chlorine that is liberated by the reaction of the two acids, although this question has not been answered definitely. Chlorine converts the metals into chlorides, AuCl_3 and PtCl_4 , which may combine with molecules of hydrogen chloride (or hydrogen plus chloride ions) to form complex acids HAuCl_4 and H_2PtCl_6 .

14 Action upon Organic Compounds

We shall describe, at this point, two of the ways in which nitric acid acts upon certain organic compounds

(a) *Certain Compounds Containing Hydroxyl Radicals* Nitric acid reacts with these compounds to form nitrates. A typical reaction of this kind is the formation of *nitroglycerine* when concentrated nitric acid reacts with glycerine. (This reaction is extremely dangerous and should never be attempted by the student.)



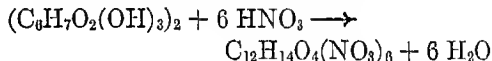
The product is called nitroglycerine erroneously since it is really a nitrate. Its scientific name is *glyceryl* (C_3H_5) *nitrate*. In the manufacturing process a mixture of concentrated nitric and sulfuric acid is used, the latter to combine with the water that is produced. If the water were not removed it would accumulate and dilute the nitric acid and the glycerine, thus slowing down the reaction. Its removal aids in the completion of the reaction.

Nitroglycerine is a liquid of extremely explosive character. It decomposes, when

warmed or when jarred, into gases, such as carbon monoxide, nitrogen, oxygen, and water vapor. The expansion accompanying the explosion amounts to an increase in volume of almost 100,000 times the volume occupied by the liquid.

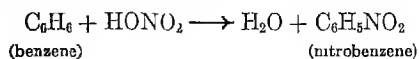
Dynamite consists of nitroglycerine absorbed in some inert material, such as sawdust or diatomaceous earth (page 533). Sometimes ammonium or sodium nitrate is added. It is less sensitive to heat and jar than pure nitroglycerine and is consequently safer to use as an explosive.

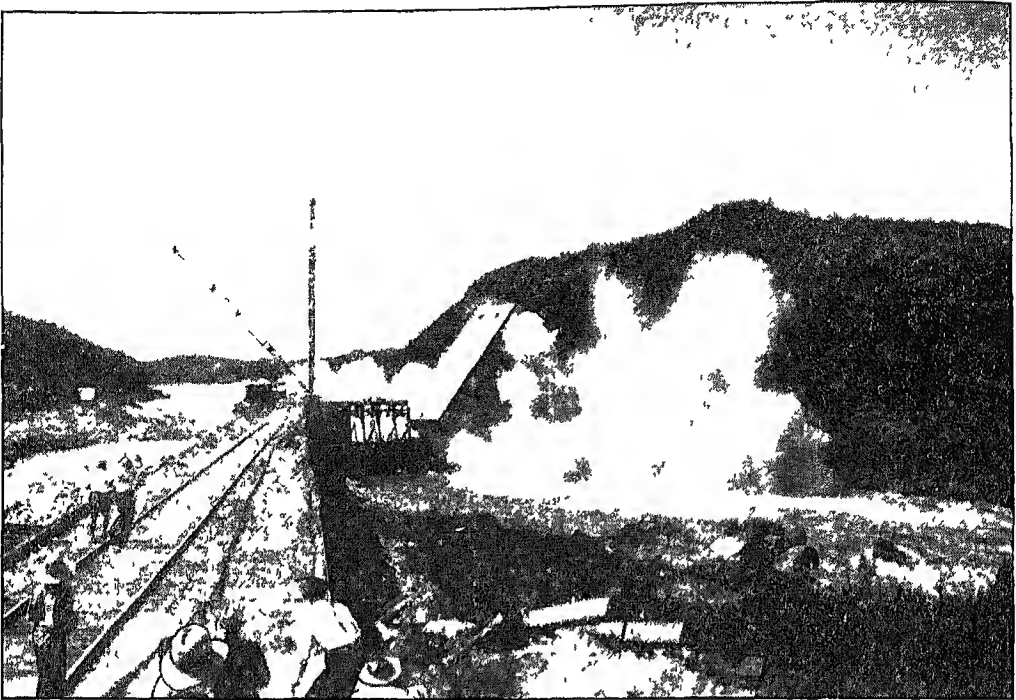
Nitric acid acts in a similar manner upon cellulose and starch to form nitrates of these substances. The reactions are similar to that used in making glyceryl nitrate, since starch and cellulose, both of which are represented by the empirical formula $(C_6H_{10}O_5)_x$, contain the OH radical in their molecules. The nitrates of these compounds are also explosives. With cellulose (of cotton or wood) the reaction is as follows:



This nitrate of cellulose is called *gun cotton*, "Smokeless powder" is made from it. If the action of the nitric acid is allowed to proceed until only three or four nitrate radicals are introduced, a non-explosive substance called *pyroxylin* is formed. This substance is the basis of the production of lacquers, artificial leather, pyralin, photographic film, artificial silk, and other substances. Gelatin dynamite contains nitrated cellulose and nitroglycerine.

(b) *Benzene and Related Compounds*
Nitric acid reacts with certain compounds of carbon and hydrogen, and with some derivatives of such compounds, to produce substances containing the *nitro* group — NO_2 . We shall illustrate this type of reaction by using benzene, C_6H_6 , and certain substances related to it. With benzene, itself, nitric acid reacts as follows:

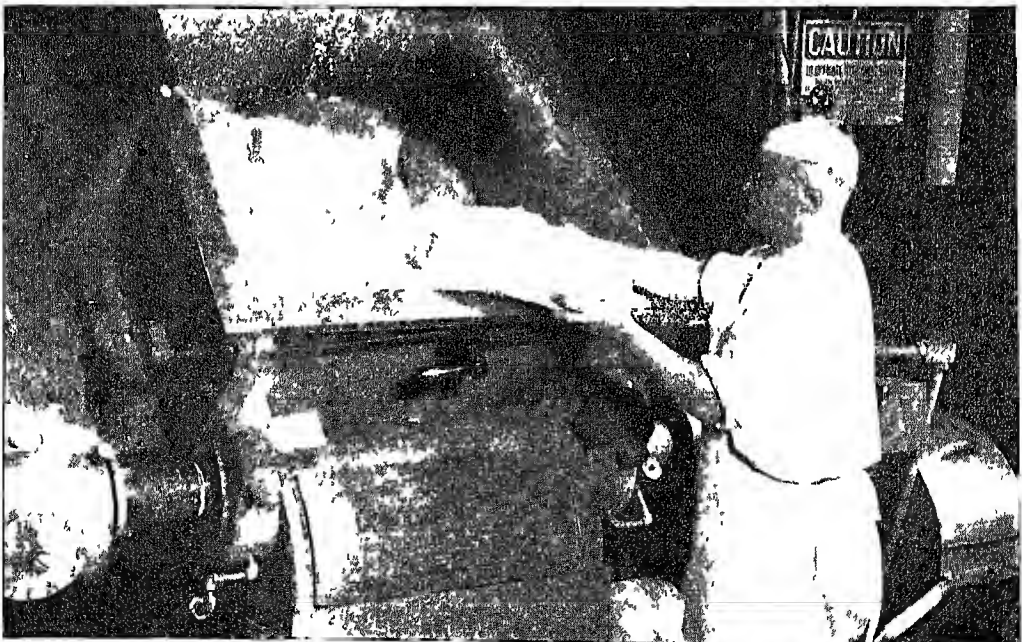




Courtesy of du Pont Company

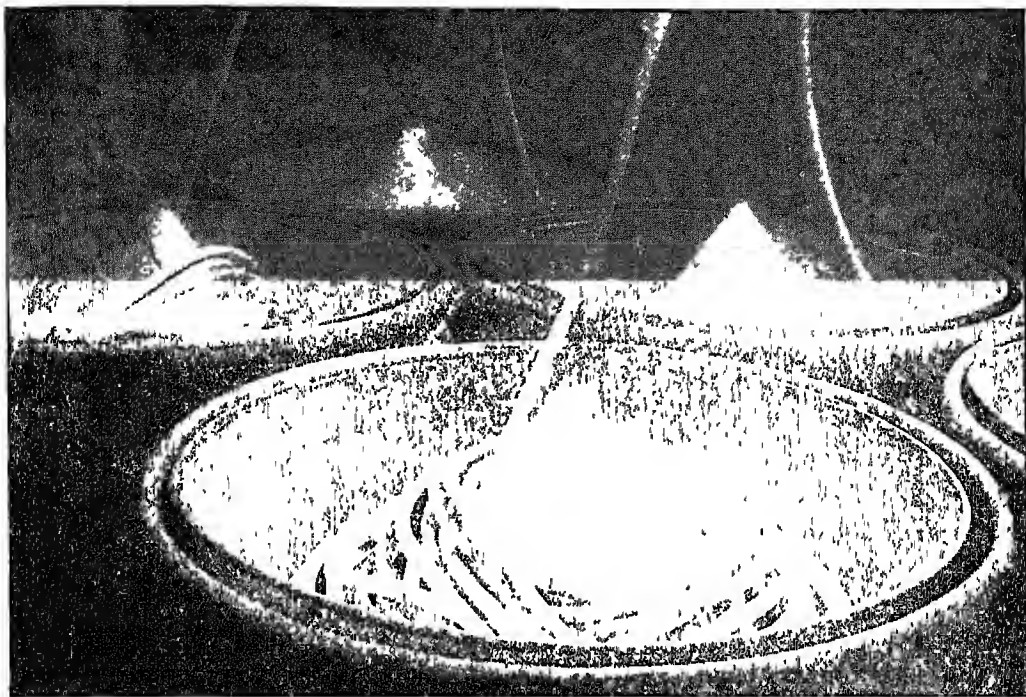
Figure 217 Use of Explosives in Peacetime

The torrential rush of the current of the Saguenay River in Conodo balked successive attempts to complete a cofferdam. The dam was built out of water, standing an end upon one bank of the river. It was then put into place by exploding one thousand pounds of dynamite in just the right spot to blow away the supports holding the dam upright.



Courtesy of du Pont Company

Figure 218 Mixing Machine in which Pyroxylin is mixed with Camphor and Solvents to Make Pyralin



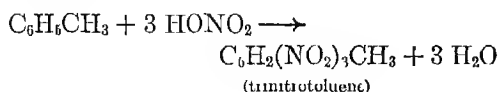
Courtesy of du Pont Company

Figure 219 Smokeless Powder

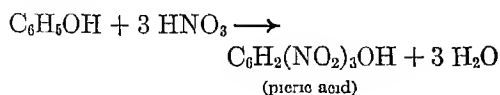
Spaghetti-like ropes of powder from one of the presses of a large Ordnance Plant. At this stage the powder is plastic. Later it is cut into cylindrical "grains."

The product, called *nitrobenzene*, is not a nitrate, since it does not contain the nitrate (NO_3) radical. The benzene molecule supplies a hydrogen atom, and the acid supplies the hydroxyl radical (OH) in forming a molecule of water. This is different from the reaction of glycerine, which supplies the hydroxyl radical instead of the acid.

Toluene (or *toluol*) ($\text{C}_6\text{H}_5\text{CH}_3$) reacts with nitric acid to form the explosive, *trinitrotoluene* (T N T)



With *phenol* ($\text{C}_6\text{H}_5\text{OH}$), which is called *carboic acid*, *trinitrophenol* or *picric acid* is produced



Picric acid is a yellow solid which is used as an explosive. The compounds of *picric acid* in which certain metals replace the hydrogen of the OH radical are extremely unstable. It is also used as a yellow dye and in the treatment of burns.

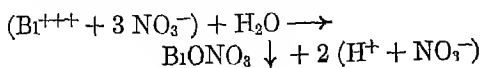
15. Uses of Nitric Acid

Nitric acid is used both as a strong acid and as an oxidizing agent. Its use in the manufacture of explosives and various cellulose nitrate products has been mentioned in the preceding section. It is also used in the manufacture of many dyes and drugs. The nitrates of the metals, many of which are produced directly from nitric acid, also have many uses.

16. The Nitrates

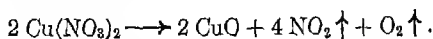
The nitrates are produced by the action of nitric acid upon the metals or upon metallic oxides and hydroxides. All the nitrates

of the metals are soluble in water, although some of them may hydrolyze to form basic salts which are slightly soluble.

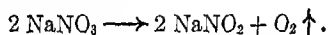


When the nitrates are heated, they are decomposed. Upon the basis of the products which they form when heated, the nitrates may be divided into the following classes

(1) Those which decompose to give the oxide of the metal. This list includes the nitrates of the heavy metals.



(2) Those which decompose to give oxygen but no oxide of nitrogen. These nitrates form nitrites of the metal.



(3) Those which undergo more deep-seated decomposition. Ammonium nitrate decomposes to give nitrous oxide and water vapor. Some of the nitrates of organic compounds, such as glyceryl nitrate, decompose explosively, forming water, nitrogen, and oxides of carbon and nitrogen.

(4) Some of the nitrates of organic compounds burn, without decomposing, when ignited in the presence of air. This is true, for example, of pyroxylin.

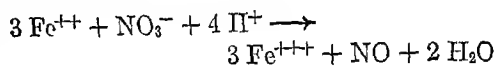
Nitrates are valuable fertilizers. The most important of those used for this purpose are calcium, sodium, and potassium nitrates. Ammonium nitrate mixed with powdered aluminum forms the explosive *ammonal*. With trinitrotoluol, it forms the powerful explosive *amitol*.

17 Test for the Nitrate Ion

The usual test for the nitrate ion uses a solution of ferrous sulfate (FeSO_4) and concentrated sulfuric acid. A freshly prepared solution of ferrous sulfate is placed in a test tube, and then 2-3 ml of concentrated sulfuric acid are added, by means of a pipette, at the bottom of the tube, so that the ferrous sulfate solution is floated on the acid (Fig-

ure 220). The two liquids should not be mixed. One or two ml of the solution to be tested for the nitrate ion is then added to the upper solution. If a nitrate is present, it will react with the sulfuric acid at the junction of the two liquids to form nitric acid. This substance, in turn, oxidizes a portion of the ferrous ion to ferric and releases nitric oxide in the process. The nitric oxide reacts with ferrous sulfate to form the brown compound $\text{Fe}(\text{NO})\text{SO}_4$. Since this compound is formed only at the junction of the two liquids, it gives a brown ring at this point. This brown compound decomposes upon heating; hence the test must be made at low temperatures. Any other ion, such as nitrite, bromide, or iodide, that reacts with sulfuric acid to give a colored product interferes with this test.

The equation for the reaction involved in this test is



CYANOGEN AND RELATED COMPOUNDS

18 Cyanogen (CN_2)

The compound called cyanogen is somewhat like chlorine in a chemical sense. It reacts, for example, with potassium and sodium to form potassium or sodium cyanide, just as chlorine in similar reactions forms the chlorides.

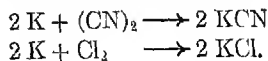
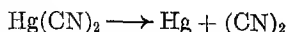


Figure 220 Test for Nitrate Ion

It is produced by heating mercuric cyanide. This reaction is similar to the decomposition of mercuric oxide.

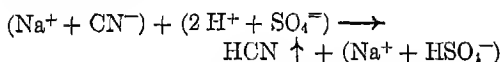


It can also be produced by means of an electrical discharge between carbon electrodes in an atmosphere of nitrogen.

Cyanogen is a colorless gas which possesses an odor reminiscent of the kernels of peach seeds. It burns to produce free nitrogen and carbon dioxide. It is an extremely deadly poison.

19 Hydrocyanic Acid (HCN)

This substance, commonly called *prussic acid*, is made by treating cyanides of the metals with sulfuric acid.



The hydrogen cyanide produced by this reaction is volatilized and the vapors are condensed by a freezing mixture. The acid is produced in nature from a substance called *amygdalin*, which is found in peach kernels, bitter almonds, and several other plant products. *Amygdalin*, itself, is not poisonous, but in many plants there is an enzyme called *emulsin*, which acts upon *amygdalin* causing it to hydrolyze. Benzaldehyde, glucose, and hydrogen cyanide are produced. This change occurs when the material is crushed and water is added. It may be prevented if the material is heated to destroy the enzyme.

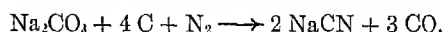
Hydrogen cyanide is a colorless liquid below 26°. It dissolves readily in water and its solution possesses the properties of a weak acid. The salts of the acid (NaCN , $\text{Ca}(\text{CN})_2$, etc.) are called cyanides. These substances hydrolyze very readily to liberate HCN . Both the acid and its salts are extremely poisonous, and when taken in even small amounts cause almost instant death.

Hydrogen cyanide is used as an insecticide. Its use should never be undertaken without great precaution and then only by persons experienced in its use. It is used in some states of the United States to execute criminals who have been sentenced to die. The salts of the acid, particularly finely divided calcium cyanide and sodium cyanide, are used as insecticides and to destroy rodents, prairie dogs, and other small animals.

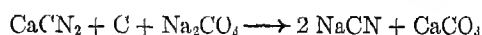
Solutions of sodium and potassium cyanides

dissolve gold and silver, forming $\text{NaAu}(\text{CN})_2$ and $\text{NaAg}(\text{CN})_2$. For this reason these salts are used in extracting gold and silver from ores in which the metals occur in the free state. The same reaction is often used in cleaning gold and silverware. The articles are dipped in a dilute cyanide bath, which removes the tarnished layer of the metal.

Sodium cyanide can be prepared directly from the nitrogen of the air by the following reaction.



It is also produced by heating calcium cyanamide with carbon and sodium carbonate (page 474).

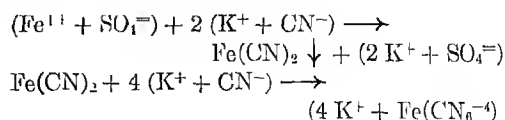


20 Cyanic Acid and Cyanates

The oxidation of potassium cyanide yields potassium cyanate, KOCN , or $\text{K}-\text{O}=\text{C}=\text{N}$. Ammonium cyanate, NH_4OCN , will be recalled (page 162) as the substance from which Wohler produced urea, the first of many successful syntheses of organic compounds by organic chemists. In potassium and ammonium thiocyanates, KSCN ($\text{K}-\text{S}=\text{C}=\text{N}$) and NH_4SCN , sulfur replaces oxygen. The thiocyanate ion (SCN^-) is useful in the detection of ferric ion (Fe^{+++}), these ions form a red compound even in extremely dilute solutions.

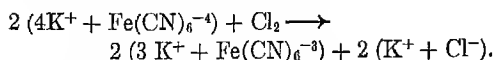
21. Complex Cyanides

Ferrous cyanide forms as a precipitate when a solution of a ferrous salt is treated with sodium or potassium cyanide. When an excess of the alkali cyanide is added, the precipitate dissolves because it is converted into sodium or potassium *ferricyanide*, $\text{K}_3\text{Fe}(\text{CN})_6$.



The ferricyanides of sodium and potassium are usually produced from by-products obtained in the destructive distillation of coal. In the gas that escapes during the distillation, a portion of the nitrogen of the coal is present as hydrogen cyanide. If the gas is passed over iron oxide, the hydrogen cyanide is converted into the cyanide of iron from which, first, calcium ferricya-

nide, and eventually sodium or potassium ferrocyanide, is produced. The ferrocyanide ion ($\text{Fe}(\text{CN})_6^{4-}$) is used as a test for ferric ion with which it forms a dark blue precipitate (Prussian blue). This substance is ferric ferrocyanide, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$. Ferrocyanides are easily converted into ferricyanides by using chlorine as an oxidizing agent.



The ferricyanide ion, $\text{Fe}(\text{CN})_6^{3-}$, contains trivalent iron. This ion is used to detect the presence of ferrous ion, with which it forms a dark blue precipitate (Turnbull's blue).

Review Exercises

- Write equations to show how
 - Ammonia is converted into nitric oxide
 - Nitric acid is converted into ammonia
 - Nitric oxide is converted into nitric acid
 - Sodium nitrate is converted into sodium nitrite
- What does the term *polymer* mean? Give an example of polymerization. Suggest some difference between polymeric and allotropic forms of substances.
- Write equations to show what happens when
 - Ammonium nitrate is heated
 - Calcium cyanamide reacts with steam
 - Cupric nitrate is heated
 - Nitric acid acts upon H_2S
 - Nitric acid oxidizes ferrous sulfate to ferric sulfate in the presence of H_2SO_4
 - Calcium hydroxide reacts with ammonium sulfate
- Illustrate by appropriate equations the chemical properties of nitric acid.
- What volume of commercial (concentrated) nitric acid can be prepared from 50 kilograms of sodium nitrate?
- What volume (standard conditions) of nitrous oxide can be prepared from 100 g of ammonium nitrate?
- Why is metallic zinc more likely to reduce nitric acid to ammonia than metallic copper?
- What volume of concentrated nitric acid could be prepared by the Ostwald process from 10 (standard) liters of ammonia? Assume that 90 per cent of the ammonia is oxidized and that all other reactions are complete.
- Identify the following laughing gas, N_2O , nitrogen tetroxide, nitrous acid, pyroxylin, aqua regia, amitol, KCN, $(\text{CN})_2$, $\text{Ca}(\text{CN})_2$, nitrosyl chloride, nitroglycerine, picric acid, $\text{C}_6\text{H}_5(\text{NO}_2)_3\text{CH}_3$.
- Show by equations two ways in which nitric acid may react with certain organic compounds, using glycerine and benzene.
- Assuming that a yield of 100 per cent can be obtained, what weight of pure hydrogen nitrate can be produced from 10 liters of liquid ammonia (sp gr, 0.62) by the Ostwald process? If this nitric acid is dissolved in water, what volume of concentrated nitric acid can be produced?
- Pure nitrous acid has never been prepared. What facts lead us to believe that this acid may exist, momentarily at least, in certain solutions?
- What is the weight of nitric acid in one liter of 6 N solution?
- If all of the chlorine is made available, what weight of auric chloride, AuCl_3 , can be produced from the chlorine contained in 10 liters (standard) of hydrogen chloride (gas)?
- One of the oxides of nitrogen contains 63.64 per cent of nitrogen. Which of the oxides is it?
- What (standard) volume of nitric oxide can be produced by the reaction of an excess of nitric acid upon 127.14 g of copper?
- Balance the following equations (Water may be formed)
 - (a) $\text{H}^+ + \text{NO}_3^- + \text{S} \longrightarrow (2\text{H}^+ + \text{SO}_4^{2-}) + \text{NO}$
 - (b) $\text{H}^+ + \text{NO}_3^- + \text{P} \longrightarrow (3\text{H}^+ + \text{PO}_4^{3-}) + \text{NO}$
 - (c) $\text{H}^+ + \text{NO}_3^- + \text{Fe} \longrightarrow (\text{Fe}^{2+} + 2\text{NO}_2^-) + \text{NO}$
 - (d) $\text{H}^+ + \text{NO}_3^- + \text{SO}_2 \longrightarrow (2\text{H}^+ + \text{SO}_4^{2-}) + \text{NO}_2$
 - (e) $\text{H}^+ + \text{NO}_3^- + (\text{H}^+ + \text{Br}^-) \longrightarrow \text{Br}_2 + \text{NO}$

References for Further Reading

(See references at close of preceding chapter.)
 Riegel, E. R., *Industrial Chemistry*, chap. VI
 Rogers, A., *Manual of Industrial Chemistry*
 Nitric Acid *Ind. and Eng. Chem.* (from ammonia), **19**, 789 (1927), **23**, 860 (1931), **26**, 1287 (1934), *Chem. and Met. Eng.*, **36**, 614 (1930), **37**, 604 (1930), (from sodium nitrate) *Ind. and Eng. Chem.*, **23**, 456 (1931), (from nitrogen and oxygen) *Chem. and Met. Eng.*, **39**, 430 (1932)

THE SULFUR FAMILY

We may judge with great accuracy the commercial prosperity of a country from the amount of sulfuric acid it consumes

LIEBIG (1840)

1 Introduction

Oxygen, sulfur, selenium, and tellurium — the B elements of group six — constitute one of the important families of elements. The physical properties of these elements are very different, oxygen, for example, is a colorless gas under ordinary conditions, while sulfur is a yellow solid. Their family relationships are revealed very strongly, however, by their chemical properties and by the similarities in composition, and often in properties, of their compounds. The following list of compounds of oxygen and sulfur shows some of the likenesses in at least the formulas of the compounds of these two elements

Oxygen	H ₂ O	CO ₂	FeO	ZnO	Na ₂ O	NaOH	As ₂ O ₃
Sulfur	H ₂ S	CS ₂	FeS	ZnS	Na ₂ S	NaSH	As ₂ S ₃

SULFUR

2 History

The word sulfur probably is derived from Sanskrit words meaning "the enemy of copper" and referring to the effect of sulfur upon copper, which is converted into a more or less worthless compound when the two elements react. Sulfur was one of the first elements known, and there is evidence that it was used for fumigating and for medicinal purposes as early as 1000 B.C. We know that it was also highly prized and widely used by the alchemists. It has long been known, also, as *brimstone*, or burning stone.

3 Occurrence

Sulfur is found in the free state in the volcanic regions of Sicily, Japan, and Mexico. Vast deposits in Texas and Louisiana are thought to have been produced by reduction of sulfur in *gypsum*, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Compounds of sulfur are more abundant in nature than is the free element. These include sulfates, the most important of which are *gypsum* and *barite* (BaSO_4), sulfides of the metals, such as *galena* (PbS), *cinnabar* (HgS), and *zinc blende* (ZnS), iron *pyrites* (FeS_2), and several ores of copper, gold, and other metals. The element is also found in certain types of organic compounds, including several kinds of proteins. The albumen of the egg, for example, contains about one per cent of sulfur. The decomposition of these substances results in the liberation of hydrogen sulfide. Sulfur is also present in many vegetable oils, such as those of garlic and mustard.

4 The Production of Sulfur

Before methods were developed for mining the sulfur deposits in the United States, most of the world's supply of sulfur came from Sicily. This is still a source of the element, but Texas produces — or at least did before World War II — about 80 per cent of the world's output. The sulfur of the deposits in Sicily is mixed with rock and soil from which it is separated by heating. The sulfur

is easily melted, and the liquid is drained away from the solid impurities with which it occurs in nature. It is then heated in an iron retort and distilled into a brick chamber, where the vapor condenses. If the temperature of the chamber is above the melting point, liquid sulfur collects on the bottom and is drawn off to be molded in the form of rods or rolls, called *roll sulfur* or *brimstone*. If the temperature of the chamber is below the melting point, the vapor condenses to give a finely crystalline powder, called *flowers of sulfur*.

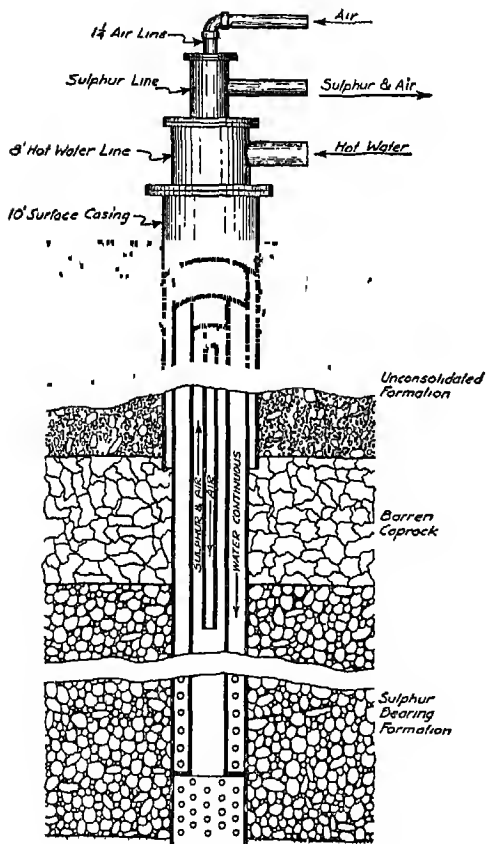
The sulfur deposits of Texas and Louisiana

are covered by several hundred feet of material of which a large part is said to be quicksand, ordinary mining operations are, therefore, out of the question. The deposits are dome-like in shape, 400–600 feet thick, and several thousand feet in diameter. Sulfur is recovered from these deposits by a process worked out by Frasch about 1900. The sulfur is melted by means of hot water and is then forced to the surface by air under pressure. Three concentric pipes are used in the well (Figure 221). Water that has been heated to about 170° under pressure is forced down the outside pipe, which is about six inches in diameter, to melt the sulfur. Hot, compressed air is forced through the smallest pipe, which is about one inch in diameter. Air, melted sulfur, and water are forced to the surface through the middle pipe by the pressure of the air and water. Almost pure sulfur—99.5 per cent—is obtained without further purification.

The annual production varies greatly because of the changing demands of the industries that use sulfur itself or its most important compound, sulfurous acid. Before the depression of 1929 and the early thirties, the annual sulfur production in the United States was about 2,400,000 long tons, and sulfur sold for \$18 per ton. The production in 1932 was only 889,695 long tons. This decrease tells the story of the economic depression as well as any data that could be quoted, for the tons of sulfur produced or consumed is, for this country at least, an index of the nation's economic prosperity. The significance of these figures depends upon the extensive use of sulfurous acid in so many widely different industries. The present annual production in the United States is about 3,000,000 tons.

5. Physical Properties

The form of sulfur that we know best is an odorless and tasteless yellow solid, usually a powdered solid called *flowers of sulfur* but sometimes in sticks called *roll sulfur*. Its



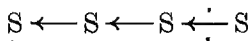
Courtesy of Freeport Sulfur Company

Figure 221. Sulfur Well



Figure 222 Loading Sulfur From a Storage Vat

density is 2.07 g per cc; its melting point is 114.5° , and its boiling point is 444.6° . At temperatures slightly above the boiling point, the vapor consists largely of molecules of S_8 , with some molecules of S_6 and S_2 also probably present. At high temperatures molecules of S_2 appear to predominate. The structure of these polyatomic molecules probably depends upon pairs of electrons that atoms of sulfur share with each other.



Sulfur appears in two allotropic, crystalline forms, *rhombic*, which melts at 112.8° , and *monoclinic*, which melts at 119° . The transition temperature at which one of these forms changes into the other is 95.5° ; above this temperature, monoclinic is the stable form, while at lower temperatures, and therefore under ordinary conditions, rhombic sulfur is stable. The densities of rhombic and monoclinic sulfur are 2.07 and 1.96 g/cc, respectively.

Monoclinic crystals can be produced by allowing melted sulfur to crystallize above the transition temperature. A considerable quantity of sulfur is melted in a porcelain dish and is then cooled, until a crust of crystals forms on the surface. This is broken and the liquid sulfur is poured off. The residue left in the dish will have formed long, transparent, needle-like crystals of monoclinic sulfur (Figure 225). After standing for some time these crystals are converted into many smaller rhombic crystals, which can be observed by microscopical examination.

Both forms of crystalline sulfur appear to be composed of S_8 molecules which are arranged in different crystal lattices, one for rhombic and one for monoclinic crystals.

Sulfur is practically insoluble in water. Both of its crystalline forms are readily soluble in carbon disulfide. In its solutions, sulfur probably exists as molecules of S_8 .

If heated to 115° , ordinary sulfur melts to give a pale yellow and very mobile liquid. When the liquid is heated to a higher tem-



Courtesy of Freeport Sulfur Company

Figure 223 Molten Sulfur from Wells

The molten sulfur is being sprayed into a storage vat, where it will cool and solidify.

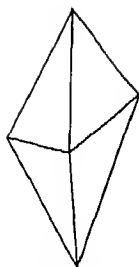


Figure 224 Rhombic Sulfur

perature, the color changes to a dark brown and the mobility decreases. These differences in the properties of the liquid indicate two (others have been described) forms of the liquid state of the element. These are called S_λ (lambda) and S_μ (mu). The latter is the darker and more viscous form. S_λ molecules contain eight atoms arranged in a ring. In S_μ the rings of eight sulfur atoms are broken, producing chains of atoms which may unite with one another to produce longer chains. Such chains, containing probably several thousand atoms, explain in large part the viscous nature of S_μ . The viscosity of the liquid reaches a maximum at about 200° , and at higher temperatures it decreases up to the boiling point. The decrease in viscosity is probably caused by the breaking up of the very long chains of atoms into shorter chains. At 200° , the liquid is so viscous that it will not flow out of an inverted tube. If liquid sulfur that has been heated almost to the boiling point is cooled rapidly by being poured into water, it is converted into a soft, amorphous, pliable mass, somewhat like rubber. This is called *plastic sulfur*. It consists of a mixture of S_λ and S_μ in a supercooled state.

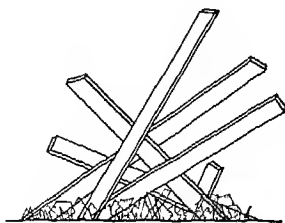


Figure 225 Monoclinic Sulfur

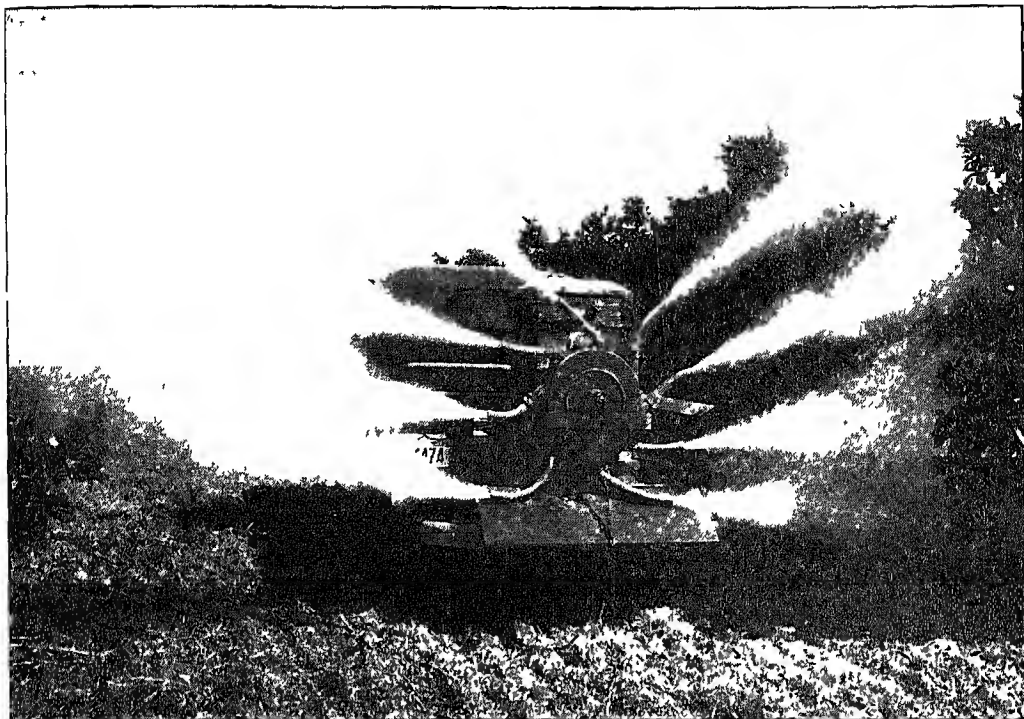
6. Chemical Properties

The two crystalline forms of sulfur have almost identical chemical properties. Just as oxygen forms oxides, sulfur combines directly with most of the elements to form sulfides. Most of the metals form sulfides when heated with sulfur. A mixture of finely divided iron or zinc and sulfur reacts very vigorously when heated and evolves sufficient heat to make the mass incandescent. Sulfur also combines with many of the non-metals, but usually less readily than with the metals, since it is a non-metal itself. It does not react with oxygen at ordinary temperatures, but burns at higher temperatures to form sulfur dioxide (SO_2). The following are representatives of its compounds with non-metals: H_2S , CS_2 , S_2Cl_2 , SCl_2 , P_4S_3 . Sulfur is converted by oxidizing agents, such as nitric acid, into SO_2 , or sulfurous acid, and upon further oxidation, into SO_3 , or sulfuric acid.

Like oxygen and the other members of the family, the sulfur atom has six valence electrons, and tends, therefore, to acquire two electrons to complete the octet. If it acquires these electrons from an electropositive element (a metal), its valence number becomes -2 . This gives the sulfide ion, S^{2-} . The sulfur atom shares electrons to give it the positive valence numbers of 4 and 6. Because of its tendency to attract electrons, sulfur is an oxidizing agent.

7. Uses

Sulfur is used chiefly in the manufacture of sulfuric acid, and also in the vulcanization of rubber (page 308). Some is used in making black gunpowder. Sulfur is also used as a fumigant. Mixed with lime, it forms a "lime-sulfur" spray that is used as a fungicide. Sulfur is used in the manufacture of many useful compounds, including sulfur dioxide, carbon disulfide, sodium thiosulfate, and the sulfide of phosphorus, P_4S_3 . It is also used in certain fertilizers to aid in converting rock phosphate, $Ca_3(PO_4)_2$, into more readily soluble compounds that plants



Courtesy of U S Department of Agriculture

Figure 226 A Multiple Nozzle Power Duster Used in a Citrus Fruit Grove for the Control of Citrus Rust Mite

can use. It is employed to some extent as an electrical insulator. Mixed with sand and heated, it forms an acid-proof cement. A substitute for slate is made from sulfur, cement, and asbestos. In organic chemistry, sulfur has many uses, especially in the manufacture of certain dyes. Medicinally, it is used in treating certain diseases of the skin. The early friction matches always contained sulfur and were often called "sulfur matches," but the free element is no longer used for this purpose; sulfides of phosphorus and antimony take its place.

HYDROGEN SULFIDE

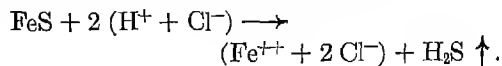
8. Occurrence

Since many organic materials contain sulfur, usually as a constituent of certain proteins, the decay or destructive distillation of these substances results in the liberation of hydrogen sulfide (H_2S). It is present in the

gases evolved when coal is distilled, in gases escaping from volcanoes, and in sewer gas. It is the substance largely responsible for the offensive odor of decomposed eggs. The waters from so-called sulfur springs also contain hydrogen sulfide and are sometimes regarded as having medicinal value because of certain minerals that they contain in solution, perhaps the foul odor and unpleasant taste, produced by the hydrogen sulfide, convince some who drink it that sulfur water must be a powerful medicine.

9. Preparation

Hydrogen sulfide is produced directly from the elements, when hydrogen is passed into boiling sulfur. It is usually prepared, however, by the action of dilute hydrochloric or sulfuric acid upon the sulfide of a metal. Ferrous sulfide is usually employed.



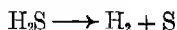
This reaction is almost complete because of the slight degree of ionization of hydrogen sulfide, and also because the gas is only moderately soluble. The hydrogen sulfide made in this way is usually not very pure. A better product is made by treating sodium sulfide, which can be prepared in a chemically pure state, with hydrochloric acid. An oxidizing acid, such as HNO_3 , cannot be used, because the hydrogen sulfide is oxidized, as rapidly as it is formed, to water and free sulfur or sulfurous acid. The Kipp generator (page 107) is often used in producing the gas for laboratory use. When needed in large quantities it can be purchased in steel cylinders. It is produced, also, by heating solid hydrocarbons — paraffin — with sulfur, which reacts with the hydrogen of the hydrocarbon to form hydrogen sulfide, leaving a residue of free carbon.

10 Properties

Hydrogen sulfide is a colorless gas, which can be condensed to a colorless liquid, boiling at -59.6° and freezing at -83° . It has a sweet, disagreeable taste and a very foul odor. The density of the gas is 1.19, as compared with air. At 15° , one volume of water dissolves a little more than three volumes of hydrogen sulfide. It is very poisonous. Continued inhalation of a very dilute mixture with air produces headache and nausea, and one part in 200 parts of air may be fatal to persons and animals. Inhalation of the gas produces paralysis of the nerve centers that regulate the functioning of the heart and lungs. A little chlorine, largely diluted with air, may be breathed as an antidote.

Chemically, hydrogen sulfide is characterized by the following properties:

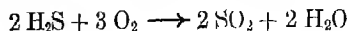
(1) It is not very stable. When heated it decomposes into the elements:



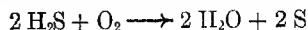
If a cold porcelain dish is held in a flame of burning hydrogen sulfide, a deposit of sulfur condenses upon the surface of the dish. The gas

decomposes into hydrogen and sulfur, but the cold dish lowers the temperature of the mixture to a point below the kindling temperature of sulfur.

(2) The gas burns in the air with a blue flame and produces water and sulfur dioxide:

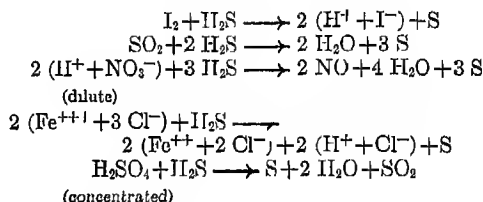


If the supply of oxygen is limited, the hydrogen is converted into water, and the sulfur is set free:

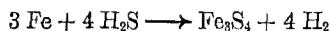


The latter reaction occurs slowly when a solution of hydrogen sulfide is exposed to the air, the sulfur separates, as the hydrogen is converted into water, giving a finely divided solid called *milk of sulfur*. This is the manner in which deposits of sulfur are produced in "sulfur springs."

(3) Hydrogen sulfide is a reducing agent. The following equations show its behavior in this respect:



(4) Hydrogen sulfide acts upon metals in a manner which is very much like the action of water. When the gas is passed over heated non-ferrous filings, hydrogen and Fe_3S_4 (compare with Fe_3O_4) are produced:



All of the metals in the electrochemical series down to and including silver readily react with hydrogen sulfide. The black tarnish on silver is produced by the reaction of the metal with this substance.

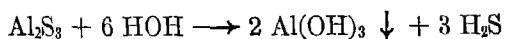
(5) The aqueous solution of hydrogen sulfide acts as a very weak dibasic acid (page 439), ionizing to form hydrogen sulfide (S^{\equiv}), and hydrosulfide (SH^-) ions. As an acid it is known as *hydrosulfuric acid*. It neutralizes bases to form sulfides and hydrosulfides (Na_2S and NaSH).

11 The Sulfides

Many sulfides occur in nature as the ores of metals (page 491). In the laboratory the

metallic sulfides are prepared by the following methods (1) by the neutralization of a hydroxide-base with hydrosulfuric acid, (2) by heating the metals with sulfur, and (3) by the interaction in solution of a salt of the metal and hydrogen sulfide. The third method is usually employed to form sulfides that are not readily soluble in water. The sulfides of the alkali metals and of the alkaline earth metals (barium, strontium, calcium, and magnesium) cannot be produced in this manner, because they are soluble, and also because, when formed, they react with water to produce the hydroxides and to release hydrogen sulfide.

Although hydrogen sulfide is only slightly ionized, its saturated solution contains a sufficient concentration of sulfide ion to exceed the solubility products of the sulfides of all the other common metals, if their ions are present even in rather small concentrations. In the presence of an acid (HCl) the concentration of the hydrogen ion is increased, and consequently the concentration of the sulfide ion is decreased. By properly regulating the amount of acid added, the concentration of the sulfide ion may be reduced sufficiently so that only the least soluble sulfides (those having the smallest solubility products) are precipitated from a solution containing all or several of the common metallic ions. The sulfides precipitated in the presence of a moderate concentration of HCl are HgS (black), PbS (black), Ag₂S (black), CuS (black), Bi₂S₃ (brown), CdS (yellow), As₂S₃ (yellow), Sb₂S₃ (orange), and SnS₂ (yellow). If these are removed by filtration, and the filtrate is neutralized by the addition of a base, the sulfide ion concentration is increased to a point where another group of sulfides precipitate. This group includes FeS (black), ZnS (white), MnS (pink), NiS (black), and CoS (black). Chromium and aluminum ions, if present, are precipitated as hydroxides, because their sulfides are almost completely hydrolyzed.



The common metallic ions are thus separated into three groups.

(1) Metals whose sulfides precipitate in acid solution.

(2) Metals whose sulfides precipitate in a neutral or alkaline solution but not in an acid solution.

(3) Metals not precipitated by hydrogen sulfide.

This is the principle that underlies the most commonly used method of separating the cations into small groups for analytical purposes.

12. Polysulfides or Persulfides

When aqueous solutions of the hydroxides or sulfides of calcium, ammonium, sodium, and potassium are heated with sulfur, the latter dissolves to form solutions of *persulfides*, sometimes called *polysulfides*. The composition of these compounds is not known definitely. The lime-sulfur sprays contain polysulfides of calcium, probably CaS₄ and CaS₅. The liquid is red in color. Ammonium polysulfide, sometimes called "yellow ammonium sulfide," is usually represented as (NH₄)₂S_x and contains (NH₄)₂S₂, (NH₄)₂S₃, (NH₄)₂S₄, and (NH₄)₂S₅.

SULFUR DIOXIDE, SULFUROUS ACID, AND THE SULFITES

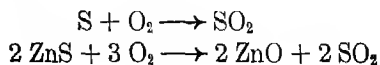
13. The Oxides of Sulfur

The two important oxides of sulfur are the dioxide, SO₂, and the trioxide, SO₃. The sesquioxide (S₂O₃), which is a blue-green solid, and the heptoxide (S₂O₇), which is a thick liquid, are not important.

14. Sulfur Dioxide, Its Preparation

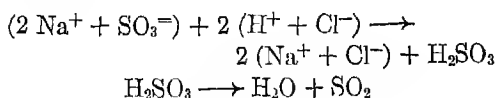
Sulfur dioxide occurs in the gases that escape from volcanoes and in the gases from the combustion of coal, which usually contains some sulfur. It is produced by the following general methods.

(1) *By burning sulfur or by roasting metallic sulfides,*

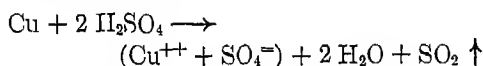


The second of these reactions illustrates the first step in the production of metals from their sulfide ores. Most of the sulfur dioxide used in the manufacture of sulfuric acid is produced by burning sulfur or roasting sulfide ores.

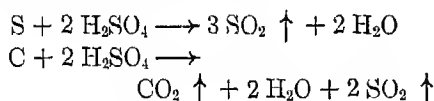
(2) *By the reaction of an acid upon a sulfite* Small quantities of pure sulfur dioxide may be prepared by treating a sulfite with an acid. Sulfurous acid (H_2SO_3) is formed first, and decomposes into water and sulfur dioxide.



(3) *By the reduction of sulfuric acid* Concentrated sulfuric acid reacts with copper and certain other metals to form sulfur dioxide. Copper is oxidized to cupric ions, and sulfuric acid is reduced to sulfurous acid, which then decomposes.

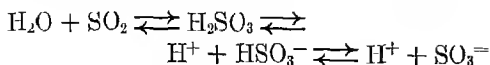


This reaction is similar to the reaction of sulfur and sulfuric acid and to the reaction which occurs when carbon is treated with hot concentrated sulfuric acid.



15 Sulfurous Acid

A solution of sulfur dioxide in water contains sulfurous acid, H_2SO_3 , which produces H^+ , HSO_3^- , and in dilute solution, SO_3^{2-} ions.



When the solution is heated, sulfur dioxide escapes and the reactions indicated above are completed toward the left. If a base, such as NaOH , is added, the reactions go toward the right, giving sodium bisulfite ($\text{Na}^+\text{HSO}_3^-$) or the normal sulfite ($\text{Na}_2^{+}\text{SO}_3^{2-}$). Because of the tendency of sulfurous acid and the sulfites to react slightly with oxygen, sulfites usually contain some sulfate.

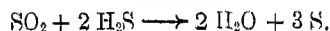
The oxidation of the sulfite ion to sulfate ion is retarded by sugar and glycerine. The acid is known only in solution.

16. Properties of Sulfur Dioxide

Sulfur dioxide is a colorless gas, 2.26 times as heavy as air, and possessing a sharp, irritating odor. It is very soluble in water, at one atmosphere and 0° , 1 volume of water dissolves approximately 80 volumes of the gas. The gas is easily liquefied (critical temp., 157°) in a freezing mixture of ice and salt at atmospheric pressure. The boiling point of the liquid is -10° and the freezing point is about -73° . Liquid sulfur dioxide is transported in steel cylinders and even in tank cars.

The chemical properties of sulfur dioxide may be summarized as follows.

(1) It acts as an oxidizing agent. This is a property of minor importance and is illustrated by the action of SO_2 upon H_2S .



(2) Sulfur dioxide is an active reducing agent. It is oxidized by such substances as KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , and even oxygen itself, to sulfuric acid. The reaction with oxygen is very slow unless it is catalyzed (page 499). In aqueous solutions the reducing agent is sulfurous acid (H_2SO_3), which is oxidized to sulfuric acid.

(3) Sulfur dioxide acts upon many kinds of colored substances to change them into colorless compounds. For some substances bleaching results from the action of sulfur dioxide or sulfurous acid as a reducing agent, but for others it is produced by the direct combination of sulfur dioxide and the colored substances to form rather unstable addition compounds. These compounds may decompose slowly and change back into the original substances when the bleached materials are exposed to sunlight. Newspapers and straw hats may turn yellow after a time, because both wood-pulp and straw are bleached by sulfur dioxide or by substances derived from it.

(4) With chlorine, sulfur dioxide forms sulfuryl chloride, SO_2Cl_2 . This compound is in a sense typical of the addition compounds that sulfur dioxide forms with many substances.

17 Uses of Sulfur Dioxide, Sulfurous Acid, and Sulfitcs

The most important use of sulfur dioxide is in the manufacture of sulfuic acid, in making this acid, sulfur is first burned to form sulfur dioxide. Large quantities are used, also, to bleach paper-making materials and wool, silk, and straw, for wool and silk cannot be bleached with chlorine (page 367). Dried fruits, canned corn, molasses, and wines are sometimes treated with sulfur dioxide for the purpose either of bleaching them or of preserving them against bacterial action, it prevents fermentation and discoloration caused by growth of molds during the drying of fruits such as peaches, apples, and apricots. Sulfur dioxide was once used as a fumigant and disinfectant, but for this purpose it has been displaced largely by formaldehyde.

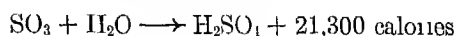
The action of sodium bisulfite as an antichlor has already been discussed (page 387). Calcium bisulfite, $\text{Ca}(\text{HSO}_3)_2$, is extensively used in preparing wood-pulp for the manufacture of paper. This substance is prepared by the action of sulfur dioxide upon calcium hydroxide, limestone (calcium carbonate), or dolomite (calcium and magnesium carbonate). Its use in the preparation of wood-pulp depends upon its ability to dissolve *lignin*, a substance which holds together the wood fibers. The material prepared by heating wood chips with a solution of the bisulfite is used in making the cheaper grades of paper.

SULFUR TRIOXIDE AND SULFURIC ACID

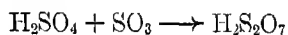
18 Sulfur Trioxide

This substance is a colorless liquid, which freezes at 17° and boils at 45° . The liquid is transformed above the freezing point, and in the presence of small quantities of water, into silky, white crystals.

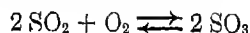
Sulfur trioxide acts as an oxidizing agent, but only with very active reducing agents. In moist air it forms a cloud consisting of tiny droplets of sulfuic acid. With water it reacts vigorously to form sulfuic acid, of which it is the anhydride.



For this reason, SO_3 is a powerful dehydrating agent. It dissolves in 100 per cent sulfuic acid to form *pyrosulfuic*, or fuming sulfuic, acid.



Sulfur trioxide is produced by the reaction of sulfur dioxide with oxygen.



The reaction is reversible, and since it is rather strongly exothermic, it is not favored by high temperatures. Even at 400° , however, 98 per cent of the dioxide is converted into the trioxide. The reaction is very slow unless catalyzed by finely divided platinum or some other material (page 503). The platinum catalyst may be prepared by dipping asbestos fibers in a solution of chloro-

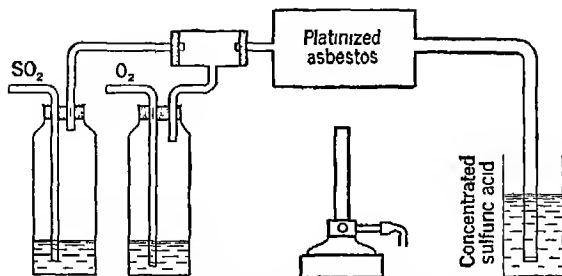


Figure 227 Laboratory Method for Producing Sulfur Trioxide and Sulfuric Acid

platinic acid (H_2PtCl_6) and heating them in a flame. The platinum compound decomposes, leaving very finely divided platinum scattered throughout the mass of asbestos. The sulfur dioxide must be carefully purified, since the platinum catalyst is easily poisoned by compounds of arsenic and other substances that are likely to be present, especially if the sulfur dioxide is prepared by roasting sulfides or pyrites (FeS_2). The temperature employed is $400^\circ\text{--}450^\circ$, and about 95 per cent of the sulfur dioxide is converted into the trioxide. This process may be carried out in the laboratory by passing a mixture containing equal volumes of sulfur dioxide and oxygen through concentrated sulfuric acid, which dries them, and then over hot platinized asbestos in a hard glass tube (Figure 227). The sulfur trioxide which escapes from the end of the tube may be collected by condensation in a receiver cooled by a freezing mixture, or it can be dissolved in concentrated sulfuric acid.

SULFURIC ACID

Sulfuric acid was known to the later alchemists. It was prepared by Basil Valentine and Glauber by the distillation of certain metallic sulfates. Commercially, it was first prepared about 1746, by a process that was the forerunner of the present lead-chamber process. A mixture of sulfur and saltpeter (KNO_3) was heated in a glass globe which also contained air and water vapor. The sulfur was oxidized to sulfur dioxide, and the oxides (NO and NO_2) of nitrogen were released. These gases then reacted with oxygen and water to form sulfuric acid.

Sulfuric acid has a more extensive industrial use than any other manufactured compound. It is by far the most widely used acid. The annual consumption in the United States fluctuates widely, but the normal amount is above 10 million tons of 62 per cent acid. During the depression year of 1932, only 4,330,000 tons were consumed. During World War II, the annual production

rose to about 10,000,000 tons. So important is this substance that the amount of it produced from year to year is a very good index of industrial prosperity.

19. Physical Properties

The anhydrous (100 per cent) sulfuric acid (or hydrogen sulfate) is a colorless, heavy, "oily" liquid, sometimes called *oil of vitriol*. Certain metallic sulfates are sometimes called *vitriols*; cupric sulfate is blue vitriol, and ferrous sulfate is green vitriol. Sulfuric acid was once obtained by distilling green vitriol and sand.

The specific gravity of 100 per cent sulfuric acid, or hydrogen sulfate, is 1.834 at 18° . When heated to about 150° , it begins to decompose, evolving water and sulfur trioxide which recombine as they cool to form fumes consisting of droplets of sulfuric acid, the decomposition at this temperature is slow and does not become pronounced until the acid is heated to about 340° . The ordinary concentrated acid of commerce contains from 93 to 95 per cent of H_2SO_4 and has a specific gravity of about 1.83. Crystals of the pure compound form at a low temperature. These melt at 10.5° . Hydrogen sulfate mixes with water in all proportions, forming solutions of sulfuric acid of different concentrations. When the concentrated acid is poured into water much heat is liberated, indicating that the acid reacts with water to form hydrates.

20. Production

Sulfuric acid is produced for commercial purposes by the *contact* process or by the *lead-chamber* process. Each of these has certain advantages and disadvantages.

21. The Lead-Chamber Process

This process is shown in Figure 228. The materials used consist of the following substances: sulfur or pyrites (FeS_2), which is burned to form sulfur dioxide, the oxides of nitrogen, $\text{N}_2\text{O}_3 \rightleftharpoons \text{NO} + \text{NO}_2$; air which supplies oxygen; and water or steam. The

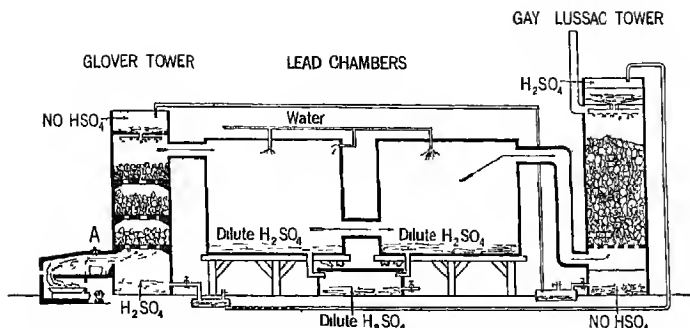


Figure 228 Lead-Chamber Plant for the Production of Sulfuric Acid
A is the "niter pot"

process is an old one; it was first used in 1746. For more than one hundred years it provided almost all of the world's supply of the acid, and even yet it competes fairly successfully with the contact process as regards the quantity produced. The lead-chamber process consists of several steps, which we shall describe separately.

(1) *The Sulfur Burners* Iron pyrites or sulfur is burned in a furnace, kiln, or burner. A large excess of air not only provides oxygen to form sulfur dioxide but leaves a surplus for later reactions in the lead chambers.

(2) The sulfur dioxide and the excess of air are next passed over the "niter pot" (A). Nitric acid, which is contained in A, or is made here by the reaction of H_2SO_4 with NaNO_3 , volatilizes and is reduced by the sulfur dioxide, forming NO and NO_2 .

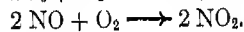
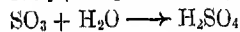
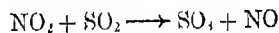


The oxides of nitrogen may also be produced by oxidizing ammonia catalytically; these oxides may be introduced directly into the lead chambers. More air may be admitted at A if necessary.

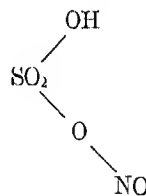
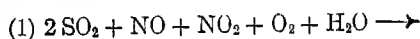
(3) The gases next pass into the Glover tower, described in (6) below. The function of this tower cannot be explained until we have first considered the reactions described in (4) and (5).

(4) *The Lead Chambers* The mixture containing sulfur dioxide, air, and the oxides of nitrogen is allowed to enter the lead chambers, where the principal reactions of the process occur. A spray of water or steam is added here. The chambers are huge rooms, lined with sheet lead, and approximately $100 \times 40 \times 40$ feet in size. From three to five chambers may be used in a plant,

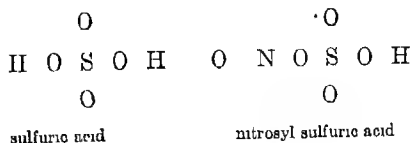
the first in the series is usually the largest. In the recently constructed plants smaller chambers are built. In some, circular towers are used instead of the lead rooms. The ultimate changes which occur here may be represented by the following equations:



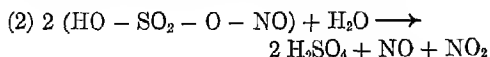
The actual reactions are considerably more complicated than these simple equations indicate. The generally accepted reactions can be described as follows:



If the quantity of water in the chambers is limited, white crystals of *nitrosyl sulfuric acid*, the product of this reaction, may be formed; these are called *chamber crystals*. The structural formulas shown below for nitrosyl sulfuric acid and for sulfuric acid explain the difference between the two acids:

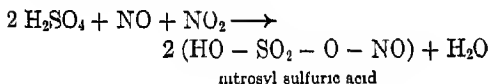


In the presence of the required amount of water, the second reaction occurs, forming sulfuric acid, and liberating the oxides of nitrogen



The oxides of nitrogen pass out of the chambers into the Gay-Lussac tower. The sulfuric acid solution (60-70 per cent) collects in the bottom of the chambers and is drained into a reservoir. A more concentrated acid cannot be produced in the chambers because it would attack the lead walls.

(5) *The Gay-Lussac Tower* The function of this tower is that of a chimney in helping to move the gases through the chambers and, more important, the recovery of the oxides of nitrogen, which are too valuable to be allowed to escape into the air. They must be returned to the process to be used over and over again. The gases escaping from the last chamber pass in at the bottom of the Gay-Lussac tower. They pass upward through tile or flint chips over which concentrated sulfuric acid is sprayed. As the acid comes into contact with the escaping gases, the following reaction occurs:



The concentrated acid, containing also the nitrosyl sulfuric acid, is drained into the reservoir at the bottom of the Gay-Lussac tower. From here it is forced (under air pressure) to the top of the Glover tower.

(6) *The Glover Tower* The acid from the bottom of the Gay-Lussac tower is forced by pressure to the top of the Glover tower, where it is sprayed over tile and comes into contact with the hot ascending gases from the sulfur burners. It is also diluted by the addition of dilute sulfuric acid. Under the influence of the heat of the hot gases from the sulfur burner, and also because of the water which is present in the diluted mixture, the reaction that occurred in the Gay-Lussac tower is reversed. (See equation (2), above.) The oxides of nitrogen are thus set free once again to begin a new trip through the lead chambers. While passing over the heated tile of the Glover tower, the acid is once more concentrated. It is this acid, from the bottom of the Glover tower, that is forced to the top of the Gay-

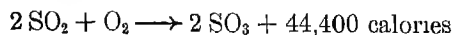
Lussac tower, there to be used in absorbing once again the oxides of nitrogen. Because there are some unavoidable losses, some additional oxides of nitrogen must be introduced into the process continuously, but this amount is small as compared with the quantity in use at any one time in the chambers.

22. Concentration of Chamber Acid

The acid made in the lead chambers is used directly for some purposes, such as the manufacture of soluble phosphate fertilizers from rock phosphate, but to prepare the more concentrated solutions used in other industries, chamber acid must be evaporated. This process may be carried out in lead pans, placed on top of the sulfur burners, but the concentration in lead cannot be carried beyond 77 per cent of H_2SO_4 , since stronger acid dissolves the layer of lead sulfate that forms on the pans and protects them against the action of the acid. The solution can be further concentrated (to about 94 per cent) in vessels made of glass, porcelain, platinum, silica, or acid-resisting Durion (iron-silicon). The vessels containing the acid may be placed on the terraced cover of an inclined flue. The dilute acid flows continuously into the top vessel, and then overflows from one vessel into the next. Since the temperature of each basin into which the acid flows is higher than that of the one above, the acid is exposed to a higher and higher temperature as it descends and becomes more concentrated. Concentration can also be effected by allowing the dilute acid to flow over bricks or tile in a tower in which hot gases are passed upward. Commercial concentrated acid is distilled from glass containers to give the chemically pure acid (98 per cent).

23. The Contact Process

The different parts of the plant used in manufacturing sulfuric acid by the contact process are shown in Figure 229. The reaction involved is



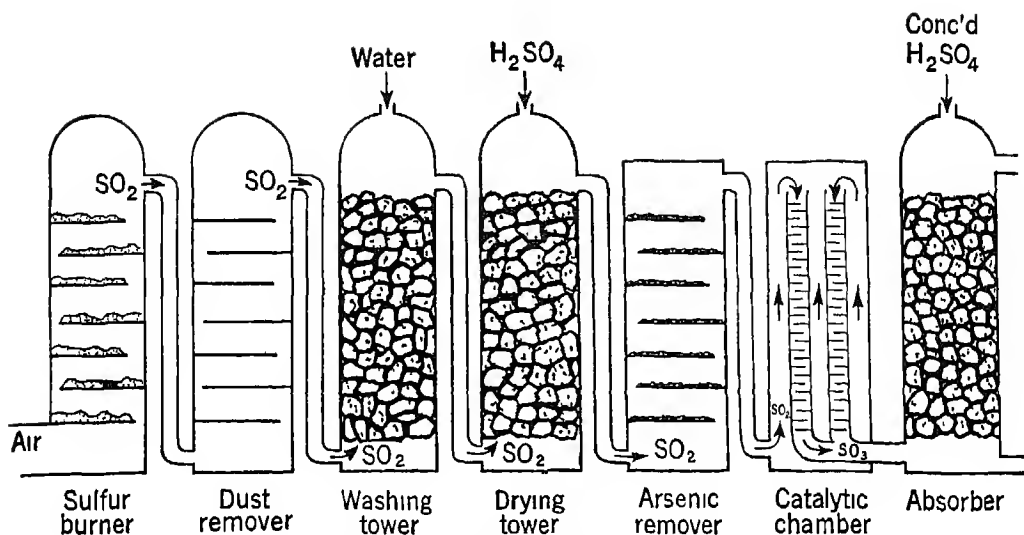


Figure 229 Diagram of a Contact Plant for the Manufacture of Sulfuric Acid

The sulfur burner shown uses sulfur or pyrite. In some burners fused sulfur is forced under pressure into the burner along with a blast of air.

Because this reaction is extremely slow, it must be catalyzed. High temperatures must be avoided because the reaction is exothermic. The catalyst first used was platinum, prepared as described on page 499, or by a similar process in which the platinum was deposited on crystals of magnesium sulfate instead of on asbestos. Ferric oxide, with which cupric oxide is mixed, and mixtures containing vanadium pentoxide (V_2O_5) have been found to be very effective, and in some respects they are more desirable than platinum because they are not so easily poisoned. The sulfur dioxide must be very carefully purified to remove impurities, especially compounds of arsenic, which act as poisons.

In the usual operation of a contact plant, liquid sulfur is forced into the burner and is burned in a blast of dry air. The gases resulting from the combustion of sulfur pass through a dust remover, and then through a scrubber where they are washed with concentrated sulfuric acid. The acid removes many of the impurities and dries the sulfur dioxide by extracting the water vapor. In order to remove any sulfuric acid that may be mixed with the gases, they are passed

through a thick layer of coke. The gases now contain sulfur dioxide, oxygen, and nitrogen. They next enter the chamber that contains the catalyst, where sulfur dioxide reacts with oxygen to form sulfur trioxide. This reaction liberates considerable heat, and unless this heat is removed, the temperature rises to a point that is unfavorable to the reaction. In order, therefore, that the reaction chamber may be cooled, the gases as they enter are first passed over the tubes that contain the catalyst before they enter these tubes and come into contact with the catalyzing materials. The temperature in the containers in which the reaction occurs must be kept fairly constant at $400^\circ\text{--}450^\circ$.

From the reaction chamber, the gases (which now contain sulfur trioxide, oxygen, and nitrogen) pass into the absorber. Here they pass up over tile or broken stoneware and are met by 97–98 per cent sulfuric acid which is introduced at the top. Unless the solution is diluted, pyrosulfuric acid, sometimes called *oleum* or *fuming sulfuric acid*, is produced, but it is possible to regulate the concentration by adding water to the solution as the trioxide is absorbed. Sulfur trioxide cannot be absorbed in water, be-

cause it forms a fog of small droplets that passes through the water without dissolving

24 Comparison of the Contact and Lead-Chamber Processes

The contact process produces any concentration of sulfuric acid from oleum to a very dilute solution. Chamber acid, on the other hand, to give the stronger solutions, must be concentrated by a difficult and tedious process of evaporation. The acid from a lead-chamber plant usually contains more impurities in the form of dissolved lead sulfate, oxides of nitrogen, and compounds of iron, arsenic, and other metals, than does that from the contact process. Nevertheless, the chamber process is still used extensively in the production of ordinary commercial "oil of vitriol," which is much in demand for the manufacture of ammonium sulfate and phosphate fertilizers, this use calls for almost one third of the acid produced annually in

the United States. The contact process requires more nearly pure sulfur dioxide than the lead-chamber process, because many impurities act as poisons to the catalyst, especially if platinum is used. This fact requires that pure sulfur be used as the source of sulfur dioxide in the contact process, while the lead-chamber process can be used to advantage with other sources of sulfur, such as iron pyrites, FeS_2 , that give a mixture of gases, when burned, that would poison a contact catalyst.

25 The Chemical Properties of Sulfuric Acid

An aqueous solution of sulfuric acid has the properties of a moderately strong, dibasic acid. If dilute, the solution reacts with metals above hydrogen in the electrochemical series to liberate hydrogen, but a concentrated solution reacts as an oxidizing agent with many metals both above and below hydrogen, forming sulfates and usually lib-

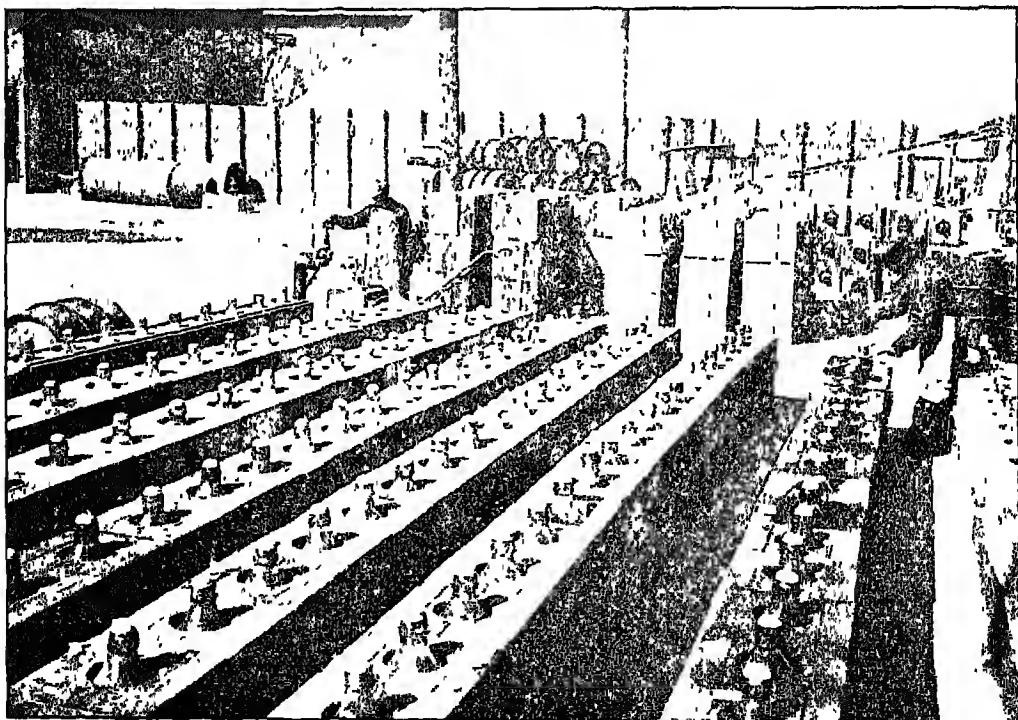


Figure 230 Filling Carboys with Acid
The acid supplied for laboratory uses is usually shipped in carboys

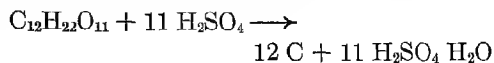
erating sulfur dioxide. The moderately dilute solution is a good conductor of the electric current, liberates carbon dioxide from carbonates, sulfur dioxide from sulfites, and hydrogen sulfide from sulfides, and reacts with the oxides and hydroxides of metals to form normal sulfates or bisulfates.

Concentrated sulfuric acid acts less rapidly upon metals to displace hydrogen than the dilute acid. This difference is caused by the smaller degree of ionization of the concentrated acid, and also by the slight solubilities of the sulfates of some of the metals in concentrated solutions of the acid, if the sulfate that first forms does not dissolve, it may cover the metal, thus preventing further action. It should be noted, however, that some metals — lead, for example — dissolve more readily in concentrated acid than in dilute, because their sulfates are more soluble in the solutions containing higher concentrations of acids. It is this condition that limits the concentration of acid made directly by the lead-chamber process (page 502).

The concentrated acid is an active oxidizing agent when heated. The reactions with carbon, sulfur, and copper (page 498) and with HI (page 347) are examples of its oxidizing action. The action of the acid in liberating volatile acids from their salts has been illustrated in the manufacture of hydrochloric (page 345) and nitric (page 481) acids.

Because of its vigorous reaction with water to form several hydrates, of which $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (or $\text{SO}_3 \cdot 2 \text{H}_2\text{O}$) is the most important, concentrated sulfuric acid is an efficient drying agent for gases that do not react with it. It also removes the elements of water (hydrogen and oxygen) from certain compounds containing them. This effect is especially pronounced if the compounds contain the two elements in the same proportion in which they occur in water. Paper, cotton, and wood, which consist essentially of cellulose, $(\text{C}_6\text{H}_{10}\text{O}_5)_x$, are charred by sulfuric acid because they are dehydrated

by it. Sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is likewise dehydrated, leaving a charred mass of carbon.



26 Uses of Sulfuric Acid

Many industries use vast quantities of this acid. Some of the more important uses are described briefly below, the figures given indicate the number of tons of 62 per cent acid used for each purpose, or in each industry, for each of two years preceding World War II. During time of war, of course, the use of sulfuric acid in those industries engaged in manufacturing munitions increases tremendously, while the use in other strictly peacetime industries is likely to decrease below normal consumption.

(1) Manufacture of fertilizer 2,447,000 — 1,970,000. The acid is used to produce ammonium sulfate and soluble phosphate fertilizers.

(2) Refining of petroleum 1,420,000 — 1,100,000. The acid is used to remove impurities from different petroleum products, such as gasoline and kerosene, the impurities, if not removed, would give the products a dark color, an unpleasant odor, and would cause deposits of waxy materials to form when the products were used as fuels or lubricants.

(3) Manufacture of chemicals 820,000 — 985,000. This includes the production of hydrochloric acid and nitric acid, the sulfates of the metals, such as aluminum sulfate, alum, cupric sulfate, and ferrous sulfate, and many other substances, such as sodium carbonate and ether.

(4) Manufacture of dyes and drugs 800,000 — 770,000. These products include different substances made from coal and coal tar products.

(5) Pickling of steel 660,000 — 700,000. Before steel is coated with enamel, tin, or zinc (galvanized), the surface is cleaned of non-rust by dipping the metal into a "pickling bath" of acid.

(6) Metallurgical uses 560,000 — 600,000. Certain metals, such as zinc and copper, are produced or purified by the electrolysis of solutions of their sulfates. To purify crude copper, an impure anode and a pure copper cathode are placed in a bath of sulfuric acid.

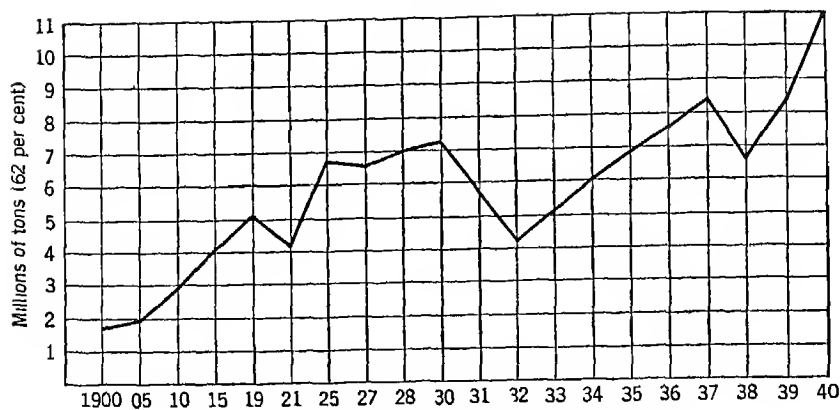


Figure 231 Annual Production of Sulfuric Acid

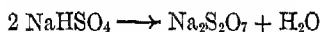
(7) Paints and pigments 200,000 — 450,000

(8) Explosives 177,000 — 220,000 Sulfuric acid is used to take up the water resulting from the reaction between nitric acid and glycerine, cellulose, toluene, phenol, or other organic compounds

(9) Nitrocellulose products, textiles, storage batteries, and other uses 408,000 — 825,000

27 Other Acids of Sulfur

(1) *Pyrosulfuric Acid*. This acid is a solid ($\text{H}_2\text{S}_2\text{O}_7$). Fuming sulfuric acid contains pyrosulfuric acid dissolved in H_2SO_4 . The salts of the acid are made by heating bisulfates



Hence, the prefix *pyro* which signifies *fire*

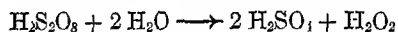
(2) *Thiosulfuric acid*. This is an unstable acid ($\text{H}_2\text{S}_2\text{O}_3$) and is unknown in the free state. The sodium salt of this acid, $\text{Na}_2\text{S}_2\text{O}_3$, commonly called "hypo" by photographers, has been described on page 387. This is the only very important salt of the acid. The additional sulfur atom in the thiosulfate radical has a negative valence of 2 and may be regarded as replacing one oxygen atom in the sulfate radical (SO_3S^-)

(3) *Persulfuric acid*. When moderately concentrated sulfuric acid is electrolyzed the following reaction, producing persulfuric acid, occurs at the anode



The electrons responsible for the negative charge of the bisulfate ions are removed by the anode when these ions are discharged. The salts of the acid can also be prepared by electrolysis, thus,

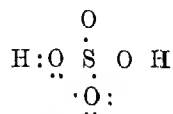
$\text{K}_2\text{S}_2\text{O}_8$ is formed by electrolyzing a solution of potassium bisulfate. These salts are vigorous oxidizing agents. When aqueous solutions slowly decompose, liberating oxygen and forming the bisulfate. When distilled under greatly reduced pressure, solutions of the acid or of ammonium persulfate form hydrogen peroxide (page 186)



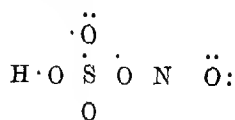
(4) *Polythionic acids*, such as $\text{H}_2\text{S}_3\text{O}_6$, $\text{H}_2\text{S}_4\text{O}_6$, and $\text{H}_2\text{S}_5\text{O}_{10}$, are also known. They are produced by reactions between hydrogen sulfide and sulfur dioxide in water, and are called trithionic, tetrathionic, and pentathionic acid, respectively. Their structures depend upon the ability of sulfur atoms to unite with each other by sharing electrons and upon the replacement of oxygen by sulfur in the sulfate radical. (See structural formulas below)

28 The Structural Formulas of Sulfuric Acid and Other Acids of Sulfur

Sulfuric acid is sometimes represented by the formula $\text{SO}_2(\text{OH})_2$. This may be further analyzed by writing the electronic formula,

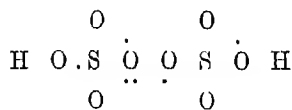


Nitrosyl sulfuric acid is

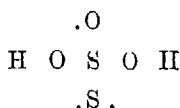


Other electronic formulas, shown below, represent the hypothetical structures of molecules of other compounds of a more or less complex nature.

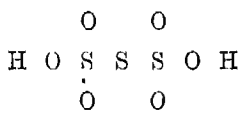
Persulfuric acid:



Thiosulfuric acid



Polythionic acids (tathionic)



29. Selenium and Tellurium

Selenium was discovered by Berzelius in 1817. The name of the element was derived from a Greek word meaning *the moon*. Selenium, which is closely related to sulfur, is found as the free element or in the combined state in free sulfur, in iron pyrites, and in certain sulfides. A common source is the dust that collects in the flues of pyrite burners. It is also obtained in the electrolytic purification of copper, nickel, and other metals that occur as sulfide ores. Its most familiar allotropic forms are red (amorphous) and gray (metallic) selenium. The latter conducts the electric current, and its conductivity depends upon the intensity of the light to which it is exposed. For this reason, it is used to regulate the flow of current in electric circuits that operate different devices, to measure the intensity of the light from stars, and for other similar purposes. It is also used to make colorless glass, which otherwise would have a slight green color due to the presence of ferrous (Fe^{++}) compounds. It may be used in larger amounts to make red glass. Selenium

is also used in the manufacture of current rectifiers, pigments, ceramics, rubber articles, and in alloys of copper and in some stainless steels.

Tellurium was discovered by Reichenstein and Klaproth about 1800, the name of the element signifies "the earth." It occurs in small amounts in nature as the free element and in the combined state. The most widely distributed compounds of tellurium are those in which the element is combined with gold, lead, and silver. These compounds are called *tellurides*.

Tellurium is usually obtained in the sludge which collects at the anode when copper and lead are purified electrolytically. It is much more metallic in appearance than either sulfur or selenium. Uses for it are in demand, since it is an abundant by-product of copper and lead refining. Some is used to make easily machined alloys of copper, and its addition to lead makes that metal more resistant and durable when used, for example, in the lead-chamber process. It is also used to improve the physical properties of rubber, and it may be added to cast iron in order to produce a wear-resistant surface.

The relationships of sulfur, selenium, and tellurium are best seen by a comparison of their compounds (Table 28). Metallic properties, melting point, boiling point, and other corresponding properties increase from sulfur to selenium to tellurium. The properties of tellurium are somewhat metallic in character, and its compounds are more like those of metals than the compounds of either sulfur or selenium. Tellurous acid is somewhat basic (as well as feebly acid) in character, while telluric acid is too weak to cause changes in the colors of indicators.

Selenium dioxide, SeO_2 , is used as an oxidizing agent in the production of several important organic compounds. Compounds of both selenium and tellurium with certain metals, as well as selenium and tellurium themselves, can be used as catalysts for several reactions, the elements, for example,

TABLE 28

Comparison of Sulfur, Selenium, Tellurium, and Their Compounds

	Sulfur	Selenium	Tellurium
Element	Melting point, 114.5° Boiling point, 444.5° Non-metallic	Melting point, 688° Boiling point, 220° Chiefly non-metallic	Melting point, 450° Boiling point, 1390° Non-metallic but shows many metallic tendencies semi-metallic in appearance
Hydrides	H ₂ S Most stable Weakest reducing agent	H ₂ Se	H ₂ Te Least stable Strangest reducing agent
Compounds with metals	Sulfides (Na ₂ S)	Selenides (CuSe)	Tellurides (CuTe)
Halogen compounds	SF ₆ , S ₂ Cl ₂ , SCl ₂ , SCl ₄ , S ₂ Br ₄ , SOCl ₂ Hydrolyze	SeF ₆ , Se ₂ Cl ₂ , SeCl ₄ , Se ₂ Br ₂ , SeBr ₄ , SeI ₄ , Se ₂ I ₂ , SeOCl ₂ Hydrolyze	TeF ₆ , TeCl ₂ , TeCl ₄ , TeBr ₄ , TeBr ₂ , TeI ₄ , TeI ₂ , TeOCl ₂ Hydrolyze
Oxides	S ₂ O ₃ , SO ₂ , SO ₃ , S ₂ O ₇	SeO ₂	TeO, TeO ₂ , TeO ₃
Acids	Sulfurous, H ₂ SO ₃ (reducing agent) Sulfuric, H ₂ SO ₄ (oxidizing agent) Hypasulfurous, H ₂ S ₂ O ₁ Thiasulfuric, H ₂ S ₂ O ₃ Dithianic, H ₂ S ₂ O ₆ Pyrasulfuric, H ₂ S ₂ O ₇ Persulfuric, H ₂ S ₂ O ₈	Selenous, H ₂ SeO ₃ (oxidizing agent) Selenic, H ₂ SeO ₄ (powerful oxidizing agent) (Both H ₂ SeO ₃ and H ₂ TeO ₃ are weaker reducing agents than H ₂ SO ₃) Tendency to form complex acids, such as dithionic acid, decreases	Tellurous, H ₂ TeO ₃ (fair oxidizing agent) Telluric, H ₆ TeO ₆ , H ₂ TeO ₄ (powerful oxidizing agent)
Salts	Sulfites, Na ₂ SO ₃ Sulfates, Na ₂ SO ₄ (Also acid salts) Sulfides and acid sulfides Also salts of more complex acids such as thiasulfates.	Selenites, Na ₂ SeO ₃ (H ₂ SeO ₃ reacts with boiling HBr to form SeBr ₄ . This shows the slightly basic character of the substance) Selenates, Na ₂ SeO ₄	Tellurites, Na ₂ TeO ₃ H ₂ TeO ₃ acts as base (TeO(OH) ₂), forming telluryl salts, as TeOCl ₂ Also neutralizes HI, acting as Te(OH) ₄ to form iodide, TeI ₄ Tellurates, Ag ₆ TeO ₁₁ , Ag ₂ TeO ₄

act as catalysts in the hardening of fats (page 116). Some applications of the elements or their compounds that have been more recently investigated include their possible uses in lubricants (as anti-oxidants), in insecticides, in certain drugs, in dyes, in

toning photographs, and in anti-knock gasolines.

Although frequently considered as among the rarer elements, almost 1,000,000 pounds of selenium and 200,000 pounds of tellurium are recovered, normally, each year.

Review Exercises

- How was the molecular formula of sulfur vapor shown to be S_8 ?
- Compare and contrast sulfur and oxygen as members of the same family of elements
- Suggest a method of preparing sulfur from each of the following: hydrogen sulfide, sulfurous acid, sodium sulfite, sodium sulfate
- Write equations which show the ionization of hydrosulfuric acid in two steps. Write equations which show other properties of hydrogen sulfide
- Write ionic equations for the following reactions:
 - $CuSO_4 + H_2S \longrightarrow$
 - $Na_2S + HOH \longrightarrow$
- Suggest a reason for using chlorine as an antidote for hydrogen sulfide in cases of poisoning produced by the latter
- Write an equation using the valence-change or electron-transfer method of balancing to show the oxidation of H_2S in a solution containing HCl and $K_2Cr_2O_7$. Chromium is reduced to Cr^{+3}
- How many liters of SO_2 under standard conditions can be prepared by burning the hydrogen sulfide produced by the reaction 100 g of FeS with HCl ?
- How many milliliters of H_2S (under standard conditions) will be required to precipitate completely the copper in 100 ml of 1 N cupric sulfate solution?
- For what reasons is sulfur classed as a non-metallic element?
- Summarize the principal occurrences, physical forms, and uses of sulfur
- Starting with a sample of galena (PbS) show how you would prepare in succession the following substances: sulfur dioxide, sodium sulfite, sodium thiosulfate, sulfur
- How would you prepare a solution of calcium bisulfite? Show by an equation how this substance reacts with hydrochloric acid
- Write equations to show how dilute sulfuric acid solution reacts with the following substances: sodium sulfide, sodium carbonate, aluminum, sodium hydroxide
- Compare the properties of sulfurous and sulfuric acids.
- What weight of sulfur must be burned to form 10 liters of normal sulfuric acid solution? Assume that SO_2 is completely converted into H_2SO_4
- Explain the function of each part of a lead-chamber sulfuric acid plant
- What conditions are most desirable in carrying out the following reaction?

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 44,400 \text{ calories.}$$

What would be the advantage and the disadvantage of using pure oxygen instead of air?
- Explain the nature of the reactions which occur in each of the following cases: (1) when sulfuric acid is used as a dehydrating agent, (2) when concentrated sulfuric acid acts upon carbon, (3) when concentrated sulfuric acid is dissolved in water, (4) when concentrated sulfuric acid reacts with sodium nitrate, (5) when a dilute sulfuric acid solution has added to it a solution of barium chloride
- Starting with sulfur state how you would prepare the following substances in succession: ferrous sulfide, hydrogen sulfide, sulfur dioxide, sulfuric acid, sodium sulfate, sodium bisulfate, sodium sulfite
- Ten grams of a sample of commercial sulfuric acid was mixed with 500 ml of water. A 25 ml sample of this solution was titrated against 0.1 normal $NaOH$ solution, and 50 ml of the solution of the base was required to neutralize it. What was the weight of H_2SO_4 in the original sample?
- How is sulfuric acid used in the fertilizer industry? Why is it used in preference to HCl or H_3PO_4 in this industry?
- How is sulfuric acid used in the manufacture of explosives? What properties of the substance make it suitable for this use?
- Why is sulfuric acid used, instead of some other acid, in liberating HCl from chlorides and HNO_3 from nitrates?
- Gypsum is a very abundant substance in nature. Why is it not used in the production of sulfuric acid? Suggest a scheme that might be used to convert gypsum into sulfuric acid
- How would you determine whether a sample

- of a given substance was sodium sulfite or sodium sulfate?
- 27 Give examples of the polythionic acids. Why is $\text{H}_2\text{S}_2\text{O}_3$ called thiosulfuric instead of thiosulfurous acid?
 - 28 Identify the following pyrosulfuric acid, oil of vitriol, nitrosyl sulfuric acid, plastic sulfur, roll sulfur, persulfuric acid, sulfurous acid, hydrogen telluride, selenic acid, hydrogen tellurite
 - 29 Ten grams of sulfur is converted into ferrous sulfide, which is then treated with hydrochloric acid. What volume of hydrogen sulfide can be produced under standard conditions? Is it necessary to know or to calculate the weight of iron or of ferrous sulfide? Explain
 - 30 What is the maximum quantity of sulfur that can be produced from 64 g of sulfur dioxide and 68 g of hydrogen sulfide when these two substances react to form sulfur and water?
 - 31 Approximately what standard volume of air is required to produce one ton of sulfuric acid from sulfur by the contact process?
 - 32 If 70,920 calories are liberated by burning one gram-atomic weight of sulfur in air to produce sulfur dioxide, what quantity of heat is liberated in the formation of 1 kilogram of sulfuric acid (100 per cent) from sulfur, oxygen, and water? (The answer will be approximate only, because the heat liberated depends to some extent upon the temperature at which the reaction occurs.)

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OTHER ELEMENTS OF THE NITROGEN FAMILY

There is no certain way of arriving at any competent knowledge except by experiment

ROGER BACON

1. Introduction

The family of elements of which nitrogen is a member occurs in the B division of group five. These elements, in addition to nitrogen, are phosphorus, arsenic, antimony, and bismuth. The atoms of each element have five electrons in their outermost group, and consequently exhibit a maximum positive valence number of 5. The negative valence number is 3. The metallic properties increase toward bismuth, which is more like a metal than a non-metal. The most important compounds of bismuth are salts, such as bismuth nitrate, $\text{Bi}(\text{NO}_3)_3$, in which it has a positive electrovalence and exists as a positive ion, Bi^{+++} , just as sodium does in its compounds. Nitrogen, on the other hand, at the top of the group is a non-metallic element in every sense.

The similarities and also some of the differences between the members of this family will be apparent as each is discussed in its turn. It may be well, however, to show the family relationships by forming a list of some of their compounds (see Table 29). We shall not attempt, at this time, to make this list complete.

From top to bottom of the different columns in Table 29 the following variations occur:

- (1) The hydrides (NH_3 , etc.) become less stable.
- (2) The chlorides are less completely hydrolyzed. NCl_3 is extremely unstable.
- (3) The oxides and hydroxides (or oxygen acids) become less acidic and more basic in character.

TABLE 29

Some Compounds of the Nitrogen Family

NH_3	NCl_3		N_2O_3	HNO_2	N_2O_5	HNO_3
PH_3	PCl_3	PCl_5	P_4O_6^*	H_3PO_3	$\text{P}_4\text{O}_{10}^*$	$\begin{cases} \text{HPO}_3 \\ \text{H}_3\text{PO}_4 \end{cases}$
AsH_3	AsCl_3	AsCl_5	As_4O_6^*	HAsO_2	As_2O_5	$\begin{cases} \text{HAsO}_3 \\ \text{H}_3\text{AsO}_4 \end{cases}$
SbH_3	SbCl_3	SbCl_5	Sb_4O_6^*	HSbO_2	Sb_2O_5	$\begin{cases} \text{HSbO}_3 \\ \text{H}_3\text{SbO}_4 \end{cases}$
BiH_3	BiCl_3		Bi_2O_6^*	$\text{Bi}(\text{OH})_3$	Bi_2O_5	HBiO_3

* These oxides are frequently represented by the simpler formulas, P_2O_3 , P_2O_5 , As_2O_3 , Sb_2O_3 and Bi_2O_5 , but the actual formulas appear to be those shown in the table.

Table 30 shows a comparison of other properties of the five members of the family

PHOSPHORUS

2 History

This element was probably discovered by Brand, in 1669, during his attempts to find the philosopher's stone. It was isolated by the reduction of phosphates found in excretions from the body. Because of its peculiar properties, especially its tendency to glow in the dark, Brand was convinced that his search had been ended. Great secrecy surrounded the methods of producing it, and it remained a rare and expensive substance until, with the development of practical uses for phosphorus, production of this element on a larger scale became possible and profitable. The method of producing phosphorus was rediscovered by Robert Boyle.

3 Occurrence

Phosphorus does not occur free in nature. The most widely and abundantly distributed

compound is calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, which occurs as the mineral *phosphorite* or *apatite*, the latter also contains calcium fluoride or calcium chloride. The common name of mineral calcium phosphate is *phosphate rock*. This is mined in Tennessee, Florida, Wyoming, Idaho, and Montana and is used as a source of phosphorus, its compounds, and phosphate fertilizers. It also occurs in many other parts of the world. Calcium phosphate is present in all soils, unless the supply has been depleted by the continued growth of crops. It is not very soluble, hence, when used as a fertilizer, it is usually converted into the more soluble acid phosphates. From this source plants obtain the phosphorus which is found, as various organic compounds and as phosphates, in their structures and products, particularly in the germs of seeds. The essential mineral from which bones are built in the animal body is calcium phosphate. Other forms of phosphorus are found in the brain, muscles, and nerves. Phosphates occur in blood, in urine and in various secretions of the body. About

TABLE 30
Some Properties of Elements of the Nitrogen Family

Element	Density	Melting point	Boiling point	Physical state	Chemical character
Nitrogen	1.2506 g per liter (standard)	-210°	-195.8°	Colorless gas	Acid-forming
Phosphorus (White)	1.82 g per ml	44.1°	280°	Wax-like solid	Acid-forming
Arsenic (Gray)	5.73	Sublimes	—	Gray, crystalline solid	Acid-forming
Antimony	6.68	630.5°	1380°	Lustrous, crystalline solid	Acid and base-forming
Bismuth	9.80	271°	1450°	Pinkish, lustrous, crystalline solid	Chiefly base-forming

one per cent of the weight of man's body consists of this element

4 Allotropic Forms

There are two familiar forms of phosphorus, *yellow* (or white) and *red*. The red variety is not a distinct form but is thought to consist of phosphorus that has been converted only partially into a *violet* modification. The pure violet allotropic modification of phosphorus can be prepared only with difficulty. It has been made by dissolving phosphorus in lead and then allowing it to separate by crystallization. It is a more stable form of the element than the yellow variety. Black phosphorus is prepared by subjecting other forms of the element to about 4000 atmospheres at an elevated temperature.

5. Yellow Phosphorus

This is the form which is most familiar, because it possesses the properties usually associated with the element. It is really neither yellow nor white, but colorless when pure. It is semi-transparent, soft and waxy, and has a garlic-like odor. It melts at 44° and boils at about 280° . It does not dissolve in water but is readily soluble in carbon disulfide, olive oil, and certain other oils and organic solvents. The vapor consists of molecules of P_4 . Yellow phosphorus is very poisonous. Its use in making matches was long ago discontinued, because the match-factory workers contracted the disease known as "phossy-jaw."

Chemically, it is very active. It combines readily with the halogens and oxygen at ordinary temperatures, and ignites in air at about 30° , its kindling point. The oxides, P_2O_3 and P_2O_5 , are produced by this reaction. It is stored under water. When exposed to water and simultaneously, it is slowly oxidized and, at the same time, some of the oxygen is converted into ozone. The glowing of phosphorus in the dark is due to light which is emitted during slow oxidation. The name phosphorus comes from this *phos-*

phorescence of the substance. This emission of light is peculiar and interesting. The light is not the result of incandescence (as in an electric lamp), for the temperature is far too low. A portion of the energy released during the reaction is liberated directly as light instead of heat.

6 Red Phosphorus

When yellow phosphorus is heated in the absence of air, it is changed into what is commonly called red phosphorus. At ordinary temperatures, the change is exceedingly slow in the dark, but the effect is readily noticeable in phosphorus that has been stored in the light for some time. The transition is much more rapid at 200° – 300° . It is also accelerated by light and by the presence of iodine. When heated, red phosphorus sublimes, forming vapor composed of molecules of P_4 . Upon condensation of the vapor, the yellow form is produced.

The properties of red phosphorus are very much different from those of the yellow variety. It does not react noticeably with oxygen or with the halogens at low tempera-

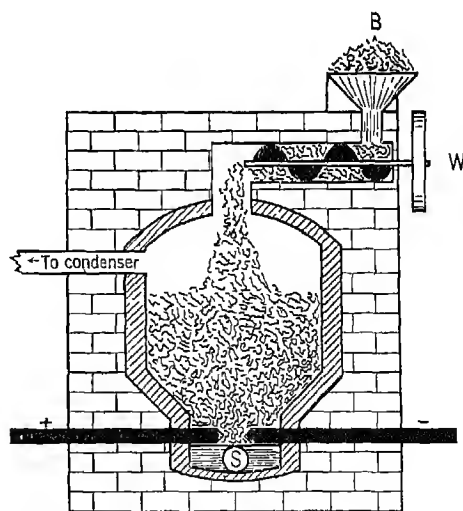


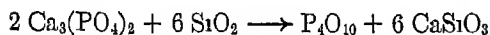
Figure 232 An Electric Furnace in Which Phosphorus is Produced

The charge, consisting of phosphite rock, coke, and sand, is fed into the furnace from B by means of the screw W. The volatilized phosphorus passes out of the furnace through the tube leading to the condenser.

tures, and ignites only when heated to about 260°. Less heat is liberated when one gram of red phosphorus burns than is liberated in the combustion of one gram of the yellow form. The former, therefore, contains less energy and is the more stable variety. It does not dissolve in carbon disulfide and is not poisonous. It melts at about 600° under increased pressure, has no odor, and is slightly more dense than yellow phosphorus (2.3 as compared to 1.82 g. per cc.)

7. Preparation of Phosphorus

The element is produced by the reduction of the phosphorus in mineral calcium phosphate or bone ash with carbon in an electric furnace (Figure 232). Heat is supplied by the resistance encountered by the current in passing between the electrodes at the bottom of the furnace. Sand (silica, SiO_2) is added to react with the calcium phosphate to form calcium silicate.

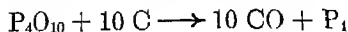


Courtesy of Monsanto Chemical Company

Figure 233 Tapping an Electric Furnace Used to Produce Ferro-Phosphorus

A stream of molten ferro-phosphorus is running from the furnace.

Calcium silicate is the *slag*, and sand acts as a *flux*. The melted slag is drawn off through the outlet (S) at the bottom of the furnace. The carbon reduces phosphorus pentoxide



The volatile phosphorus escapes as vapor, and is condensed to a liquid, thus it is separated from the carbon monoxide, which escapes from the furnace with it. The liquid phosphorus is then run into molds and cast into sticks.

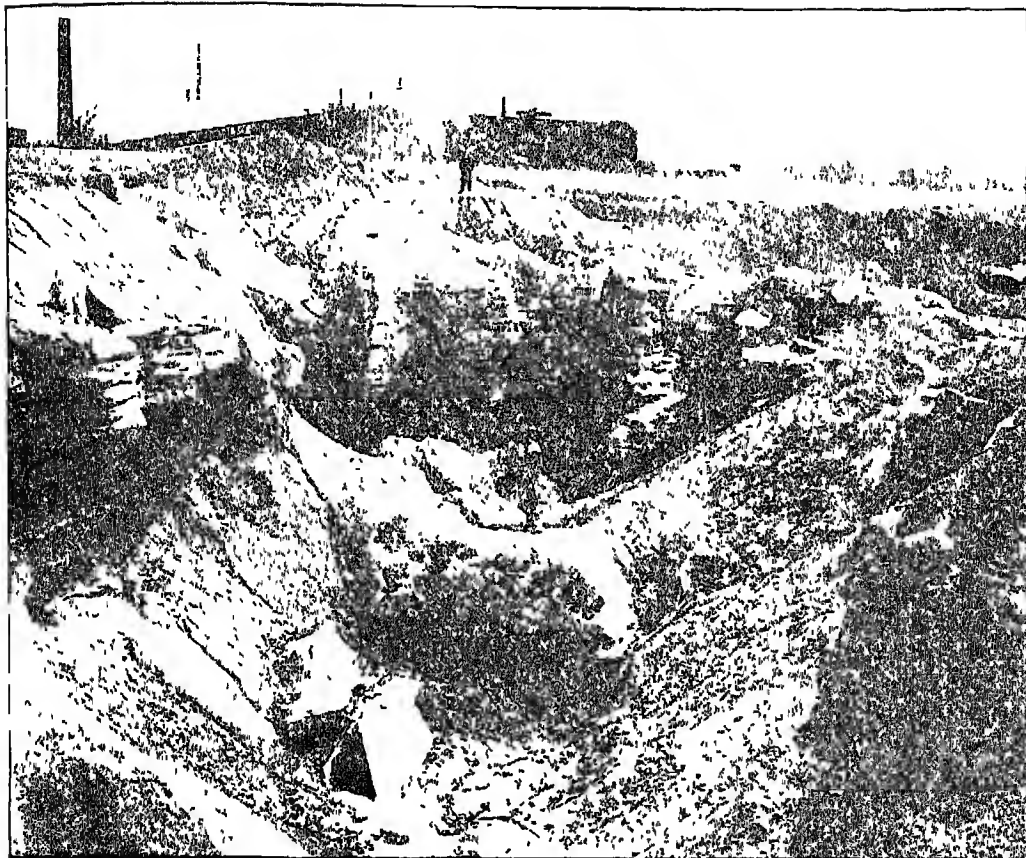
8. Uses of Phosphorus

When it burns in moist air, phosphorus forms phosphorus pentoxide, P_4O_{10} , which reacts with water to form a fog composed of small droplets of a solution of phosphoric acid. This cloud can be used as an effective smoke-screen. Phosphorus is also used in making incendiary shells and grenades. The use of phosphorus, and its compounds, in the manufacture of matches was introduced about 1825. The element is also used in producing phosphor-bronzes and in manufacturing certain compounds of phosphorus, such as the chlorides, PCl_3 and PCl_5 , and the sulfide, P_2S_5 . Small quantities are utilized in manufacturing a rat poison.

9. Matches

The ordinary friction match depends upon the ease with which red phosphorus or compounds of phosphorus can be ignited. The first matches of this kind contained white (or yellow) phosphorus, but its use was later prohibited by laws and other regulations in all countries, because it caused disastrous fires and was a source of danger to the health of employees in the match factories. Phosphorus causes necrosis — decay — of bones, usually the bones of the jaw, if first enters the teeth as phosphorus vapor through decayed portions, and its action is then extended to the bones in which the teeth are set.

The type of match that is "struck" by rubbing its head upon almost any type of surface (the more friction the better) contains the following materials: a layer of paraffin on the "head-end" of the stick, an oxidizing agent, such as potassium



Courtesy of Monsanto Chemical Company

Figure 234 Phosphate Rock
The out-cropping of rock is called "horse"

chlorate, and combustible substances (paraffin and sulfur). Glue is also present in the head, this acts as a binding agent. The head also contains some filler such as clay, starch, or plaster of Paris, and sometimes an abrasive material, such as fine sand or ground glass. The tip on the head of the match contains, in addition to the substances in the rest of the head, phosphorus sesquisulfide, P_2S_5 . This substance is ignited when it is heated by the friction produced when the match is rubbed against some object. The combustion of this substance then starts the reaction between sulfur (or some other combustible material) and the oxidizing agent ($KClO_3$). This, in turn, ignites the paraffin, and eventually the wood, itself, begins to burn.

The safety match is "struck" by rubbing it on the side of the box. The head of the match con-

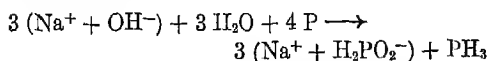
tains an oxidizing agent, such as potassium chlorate, and a readily combustible substance, the latter is usually antimony sulfide (Sb_2S_3). The side of the box is coated with a mixture of glue, an abrasive (to increase friction), red phosphorus, and an oxidizing agent. This match is somewhat safer than the "strike anywhere" variety, since the material in the head of the match is not easily ignited, except on the special surface provided on the box. It is really the phosphorus on the box which first ignites when the match is "struck."

10 Phosphine

This compound, which has the formula PH_3 , corresponds to ammonia, NH_3 . It is a very poisonous gas and possesses an offen-

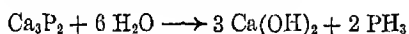
sive odor. Phosphine reacts with hydrogen chloride to form phosphonium chloride, PH_4Cl , which, although it corresponds in composition to ammonium chloride, NH_4Cl , does not produce PH_4^+ ions in solution. Instead, it decomposes, in the presence of water, to form phosphine.

Phosphine is usually prepared by heating a solution of concentrated sodium hydroxide in which small particles of yellow phosphorus are suspended.



Air is first removed from the flask (Figure 235) by passing a stream of illuminating gas through it. Phosphine is formed and escapes through the delivery tube which has its outlet just below the surface of the water. As the bubbles escape into the air, the gas is ignited, and the oxides which are formed float away in the form of rings. It is thought that another hydride (P_2H_4) is produced in small quantities along with PH_3 , and that this second hydride is responsible for spontaneous combustion, which occurs as soon as the gas comes into contact with air.

Phosphine is also prepared by the reaction of water with calcium phosphide.



11. Chlorides and Other Halides

The chlorides, PCl_3 and PCl_5 , are representative of the compounds that phosphorus

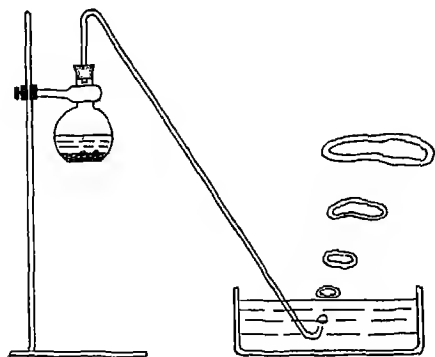
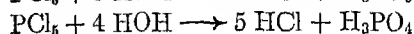
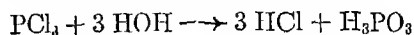


Figure 235 The Production of Phosphine and Its Spontaneous Combustion in the Air

forms with all of the halogens. All of these halides are prepared by the direct combination of the elements. Phosphorus tri-iodide, for example, is formed by grinding red phosphorus and iodine together in a mortar. The chlorides are the most important of the halides of phosphorus. The trichloride is a fuming, colorless liquid, the pentachloride is a yellow solid. They are used in the preparation of certain compounds in organic chemistry. Both the trichloride and pentachloride react with water (hydrolyze) to form HCl and an acid of phosphorus.



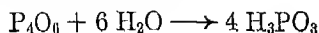
Similar reactions of PBr_3 and PI_3 with water will be recalled as methods of producing pure hydrobromic and hydroiodic acids (page 347).

12. Oxides

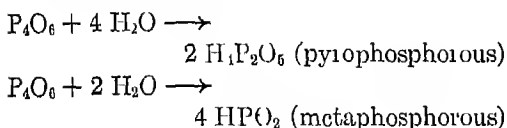
The two best known oxides of phosphorus are the anhydrides of phosphorous and phosphoric acids. Both oxides are white solids. Their simple formulas are P_2O_3 and P_2O_5 , and these are frequently used to represent the oxides, but the actual molecular formulas appear to be P_4O_6 and P_4O_{10} , respectively. The latter, usually called the *pentoxide*, is produced by burning phosphorus — either red or yellow — in an excess of oxygen. The *trioxide* is produced, along with some pentoxide, if the supply of oxygen is limited. It can be separated from the pentoxide by heating the mixture to about 175° , at which temperature the trioxide is readily vaporized, the pentoxide is less volatile. The trioxide is a reducing agent, but the pentoxide is very stable and, ordinarily, shows neither oxidizing nor reducing properties, although it can be reduced, as in the production of phosphorus in the electric furnace. Because of the pronounced tendency of the pentoxide to react with water, forming phosphoric acid, this oxide is a powerful drying agent. There is also a tetroxide, P_2O_4 .

13. Phosphorous Acids

Phosphorus trioxide reacts with water to form phosphorous acid



The acid is usually prepared, however, by the hydrolysis of PCl_3 . It is an active reducing agent and a weak *dibasic* acid, the third state of the ionization is negligible, even in dilute solutions. Its sodium salts (phosphites) are NaH_2PO_3 , Na_2HPO_3 . The phosphites are used in medicine. The formula H_3PO_3 is assigned to the compound called *orthophosphorous acid*. In the presence of limited amounts of water and under the proper conditions of temperature, the following phosphorous acids — theoretically at least — may also be formed

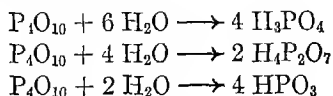


Only the orthophosphorous acid is well known

The salt NaH_2PO_2 , which is made in the preparation of phosphine, is an acid salt of *hypophosphorous acid* (H_3PO_2). All the salts of this acid are the products of the first stage of ionization — the acid is monobasic. The *hypophosphites* are used in medicine.

14. Phosphoric Acids

There is no acid that corresponds exactly to the hypothetical hydroxide, $\text{P}(\text{OH})_5$, as H_3PO_3 corresponds to $\text{P}(\text{OH})_3$. There are, however, three acids of which the oxide P_4O_{10} is the anhydride, and which may therefore be called phosphoric acids. These three acids differ in composition and in properties, their relations to the anhydride are shown by the following equations



The acids are named *ortho*-, *pyro*-, and *meta*-phosphoric acid, respectively

15. Pyrophosphoric and Metaphosphoric Acids

The prefix *pyro* refers to the formation of pyrophosphoric acid by *heating* orthophosphoric acid to 200–250°



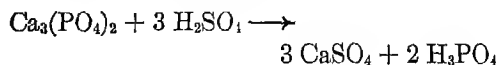
If the ortho acid is heated to a higher temperature (400–500°), metaphosphoric acid is produced



Both of these acids are white, crystalline compounds. Pyrophosphoric acid is tetrabasic. The sodium salt of this acid, $\text{Na}_4\text{P}_2\text{O}_7$, is used in some soaps and soap powders as a water softener. Metaphosphoric acid can be melted, and the liquid upon cooling forms a glass-like solid, sometimes called *glacial phosphoric acid*, which dissolves the oxides of metals. The compounds thus formed — phosphates of the metals — have different colors, depending upon the metals involved. Some of the tests for certain metals are based upon the formation of such compounds. Metaphosphoric acid exists in different polymerized molecular forms, such as $(\text{HPO}_3)_2$, $(\text{HPO}_3)_3$, and $(\text{HPO}_3)_6$. Sodium hexametaphosphate, $\text{Na}_6(\text{PO}_3)_6$, is used in softening water.

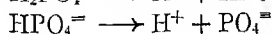
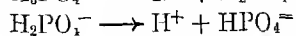
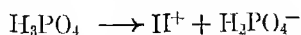
16. Orthophosphoric Acid

This is the most important of the three phosphoric acids. The pyrophosphoric and metaphosphoric acids are readily converted into this form in the presence of water. Anhydrous orthophosphoric acid (hydrogen phosphate) is a colorless, crystalline substance (m p 42°). The usual form in which it is provided for use is a syrupy solution containing about 85 per cent of H_3PO_4 . This acid is prepared by the action of concentrated sulfuric acid upon calcium phosphate. The calcium sulfate precipitates and may be removed by filtration



It is also produced for commercial use by burning the vapor of phosphorus in the air and allowing the oxide formed by the combustion to react with water. In the laboratory, it can be produced by the oxidation of red phosphorus with nitric acid.

Orthophosphoric acid is tribasic and is ionized to a moderately high degree (page 237). The third stage of ionization occurs only slightly except in a very dilute solution.



17 Salts of Orthophosphoric Acid

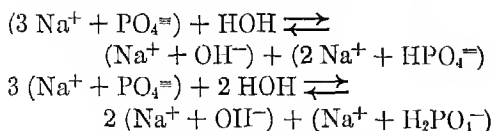
Corresponding to the three stages of ionization, the acid forms three series of salts. The sodium salts and the names commonly applied to them are as follows:

NaH_2PO_4 Monosodium phosphate
Primary sodium phosphate
Dihydrogen sodium phosphate

Na_2HPO_4 Disodium phosphate
Secondary sodium phosphate
Monohydrogen sodium phosphate

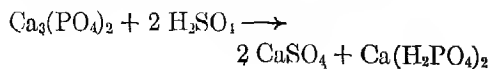
Na_3PO_4 Trisodium phosphate
Tertiary or normal sodium phosphate

Because of the very slight degree of ionization of the HPO_4^{2-} and H_2PO_4^- ions, normal sodium and potassium phosphates are rather strongly hydrolyzed in aqueous solutions.



Because it reacts in this manner to form a solution of sodium hydroxide, trisodium phosphate is used in some soap powders and also alone as a cleansing agent.

When normal calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) is treated with sulfuric acid the primary (acid) phosphate is produced.



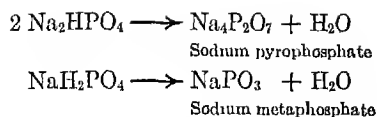
The normal phosphate is practically insoluble, while the primary salt is much more soluble. The latter is commonly called *superphosphate*. If the normal salt is used as a fertilizer, it is not readily available for plant nutrition because it is very slightly soluble. It is for this reason that phosphate rock is treated with sulfuric acid (page 505) in the manufacture of fertilizers. The primary salt is more readily soluble and is therefore more available for plant use. The calcium sulfate is not separated, but forms a part of the prepared fertilizer, and probably is of some value itself.

Ordinary superphosphate fertilizers contain only about 16 per cent of available and useful fertilizing ingredients. A more concentrated form, containing up to 50 per cent of available P_2O_5 , is more desirable from the point of view of transportation costs. The less concentrated form is not so likely, however, to cause damage to plants, the more concentrated form must be distributed over the soil more carefully and should be diluted with soil or other fillers before it is used. During a recent year, 3,300,000 tons of rock phosphate in the form of superphosphate fertilizers and 80,000 tons of the powdered, untreated phosphate were used in the United States. Close to 300,000 tons were used to make phosphorus, phosphoric acid, and other compounds of the element.

Microcosmic salt ($\text{NaNH}_4\text{HPO}_4$) is an example of a *mixed* salt. The mixed salt, MgNH_4PO_4 , is formed, as a white crystalline precipitate, in one of the commonly used tests for either magnesium or phosphate ion. The heavy metals, such as silver and lead, form only normal phosphates. These are only slightly soluble.

Phosphoric acid is used in soft drinks and in making certain fertilizers, such as ammonium phosphate. Its salts are used as fertilizers, in baking powders (page 384), as cleansing agents, and in softening water, in fireproofing fabrics, in weighting silk, in making yeast, and in clarifying sugar solutions.

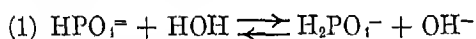
Salts of pyrophosphoric and metaphosphoric acids are prepared by heating acid salts of orthophosphoric acid.



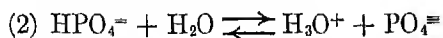
Sodium metaphosphate is very stable. The liquid formed when the salt is melted cools to give a glass-like solid. When heated with oxides of certain metals, it dissolves them, forming variously colored substances that can be used as a means of identifying the metals whose oxides are dissolved. Thus, cobaltous oxide (CoO) and sodium metaphosphate form the mixed phosphate NaCoPO_4 , when they are heated together. This compound has a beautiful, clear blue color.

18 Salts of Phosphoric Acid as Buffers

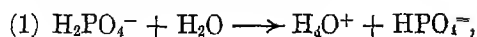
Let us consider the reactions that occur in aqueous solutions of the three sodium salts of orthophosphoric acid — NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 . In a solution of the normal phosphate, PO_4^{3-} ions are liberated. Since the ion HPO_4^{2-} is only very slightly ionized, the phosphate ion, PO_4^{3-} , tends to react with water to form HPO_4^{2-} and OH^- ions. Therefore, the concentration of the hydroxyl ion increases, and the solution of the normal phosphate is strongly alkaline. A solution of the secondary phosphate, Na_2HPO_4 , contains HPO_4^{2-} ion which reacts with water as a base:



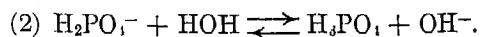
It may also act as an acid



But HPO_4^{2-} is a much stronger base than acid, and hence a solution of the secondary phosphate is also alkaline in reaction, but it is not so strongly alkaline as a solution of trisodium phosphate. Primary sodium phosphate, NaH_2PO_4 , forms, in a solution, H_2PO_4^- ions which can act as an acid



or as a base,



But H_2PO_4^- is a stronger acid than base; and hence it produces more H_3O^+ ions (re-

action 1) than OH^- ions (reaction 2). Consequently, a solution of the primary phosphate is slightly acid in reaction.

For the reasons explained above, solutions of primary and secondary phosphates are excellent *buffers* which can be used to control the concentration of the hydrogen ion. In the presence of HPO_4^{2-} and H_2PO_4^- ions, the concentration of the hydrogen ion does not change much, if any, from a definite value, even though small quantities of acids or bases may be added to the solution. If hydrogen ions are added, they will combine with HPO_4^{2-} to form H_2PO_4^- , and if OH^- ions are added, they will react with protons supplied by H_2PO_4^- and thus be converted into molecules of water.

19 Phosphorus and Nitrogen

Phosphorus is more closely related to nitrogen, in a chemical sense, than any of the other members of the family. This relationship is evident in a number of ways. The oxides of phosphorus resemble N_2O_3 and N_2O_5 in reacting with water to form acids, they do not act as bases. Both elements, acting as non-metals, form similar compounds with the metals, phosphorus forms phosphides, and nitrogen forms nitrides (Ca_3P_2 and Mg_3N_2). Neither element forms salts in which it acts as a cation. Nitrogen's properties, as a non-metal, are somewhat more strongly marked, however, than those of phosphorus. Phosphorus, for example, shows a much stronger tendency to react with other non-metals, forming very stable compounds with oxygen, and fairly stable compounds with chlorine and sulfur. The stability of these substances is great in contrast with the instability of the corresponding compounds of nitrogen. Nitric acid and the nitrates are active oxidizing agents, phosphoric acid and the phosphates are reduced only with difficulty.

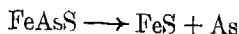
ARSENIC

Arsenic compounds have long been known. They were the poisonous substances most

often used in the poison plots of antiquity. The alchemists were acquainted with the oxide, As_4O_6 . Certain brightly colored arsenic compounds were used by the Greeks and Romans as pigments. The most important use of arsenic compounds today depends upon their poisonous character, for they are employed as insecticides.

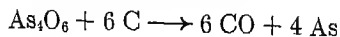
20. Occurrence

Small quantities of arsenic are found naturally in the free state, but the principal sources are the sulfur compounds *orpiment* (As_2S_3), *realgar* (As_2S_2), and *arsenopyrite* (FeAsS). Wherever we find sulfide ores of the metals, such as lead, copper, zinc, and iron, there too we are likely to find sulfur compounds of arsenic. Iron pyrites (FeS_2) always contains some arsenic, which tends to poison the catalyst in the contact process of manufacturing sulfuric acid. Metals prepared from sulfide ores usually contain some arsenic, unless they are carefully refined. Most of the arsenic produced in America comes from the dust that collects in the flues of copper-ore smelters. Some is also obtained from the dust that collects in the process of smelting the ores of other metals, such as lead and gold. When the sulfides of these metals are roasted, preparatory to their reduction to the metals, arsenic sulfide is converted into the oxide, As_4O_6 , which is frequently written as As_2O_3 , the simplest formula. This oxide is volatile and condenses in the dust that collects in the flues of the furnaces. Some free arsenic may also be volatilized, especially in furnaces in which arsenopyrite is roasted.



21. Preparation

The element is prepared by reducing the trioxide (As_2O_3) with carbon.

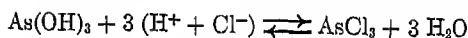


22. Properties

Arsenic has an appearance something like

that of a metal, but lacks strength and can be easily broken up into small particles. It is a dark gray, crystalline solid. It sublimes readily, giving a yellow, poisonous vapor which has the odor of garlic. The molecules of the vapor correspond to the formulas As_4 or As_2 , depending upon the temperature. It occurs in at least three allotropic forms, but gray arsenic is the only one of any importance, the others are very unstable, changing quickly, even at ordinary temperatures, into gray arsenic.

Chemically, arsenic resembles phosphorus in many ways. The main difference between the properties of the two elements is a slightly greater tendency of arsenic to act as a metal. This is by no means a pronounced tendency. It is best illustrated by the slightly basic character of the trioxide and of the compound which this substance forms with water. This substance is a weak acid, H_3AsO_3 , but it must also possess at least very slightly basic properties, and therefore acts as a hydroxide, $\text{As}(\text{OH})_3$. With highly concentrated solutions of hydrochloric acid it reacts as a base.



This reaction is reversible and under ordinary conditions tends to run strongly to the left because of the extremely weak basic character of $\text{As}(\text{OH})_3$. To force it toward the right, the concentration of HCl must be very great. In other words, the concentration of OH^- ions produced when $\text{As}(\text{OH})_3$ acts as a base is very small, hence the concentration of the H^+ ion must be very large in order that the ion product of water, $[\text{H}] \times [\text{OH}^-] = 1 \times 10^{-14}$, may be exceeded to an appreciable extent, and water molecules may be formed. Arsenic trichloride resembles the chlorides of phosphorus more than it does the chlorides of the metals, it is, for example, almost completely hydrolyzed.

Arsenic oxidizes but slowly at ordinary temperature in moist air. It ignites at about 200° , forming a white smoke which consists of the trioxide. It burns in chlorine to form the trichloride, AsCl_3 , and combines with the other halogens to form similar compounds. It also reacts directly with sulfur. With the metals it forms *arsenides*. It is a reducing

agent; nitric acid, for example, oxidizes it to arsenic acid (H_3AsO_4). Unlike the metals, it will not displace hydrogen from HCl . But in the presence of oxygen it does dissolve in a concentrated solution of this acid, probably because it is first oxidized to the oxide, As_4O_6 , which then reacts as a weak base with the acid, forming the soluble chloride, AsCl_3 , and water.

23. Uses

Free arsenic is used in manufacturing certain bronzes and other alloys, lead shot, and compounds of the element. In making shot, arsenic is added to form harder and more nearly spherical drops of lead. Shot is made by pouring melted lead through a screen which breaks up the liquid into a great many small drops. When pure lead is used the liquid drops change very quickly to the solid state. When arsenic has been added, the drops solidify more slowly, allowing more time for the small masses of liquid lead to attain spherical form. The presence of arsenic in other alloys increases the luster, strength, hardness, fluidity, and resistance to certain chemical actions.

24. Arsine

Analogous to phosphine and ammonia is the arsenic compound, arsine (AsH_3). This substance is a gas which has a "garlic" odor and is extremely poisonous. Unlike ammonia it does not react with water, in fact, it does not even dissolve, and it forms no salts similar to the ammonium salts. It is unstable, decomposing into the elements when only moderately heated. It burns with a slightly blue flame to form water and to deposit arsenic, if the supply of oxygen is limited, but in an excess of air the arsenic is oxidized to As_4O_6 . Arsine is produced by the action of atomic hydrogen upon the compounds of arsenic.

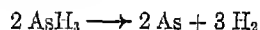


The atomic hydrogen is usually supplied by the action of an acid upon a metal, such as

arsenic-free zinc, in the presence of the arsenic compound.

25. Marsh's Test for Arsenic

The test for arsenic which is very widely used depends upon the formation and decomposition of arsine (Figure 236). Hydrogen is generated in the flask, dried by means of calcium chloride in a drying tube, and ignited at the end of the glass tube. The substance to be tested for the presence of arsenic is then introduced through the thistle tube. If this substance contains arsenic, arsine is formed and escapes along with the hydrogen. When the glass tube is heated at some point between the outlet and the drying tube, the arsine is decomposed at this point, and a deposit of arsenic is formed just beyond the heated portion of the tube. This deposit is in the form of a bright, metallic mirror. The zinc and hydrochloric acid should be checked for the presence of arsenic before the material to be tested is placed in the flask.



26. Oxides

Arsenous oxide, better known as the trioxide, As_2O_3 , is the substance commonly referred to as "arsenic" or "white arsenic." It is produced by the combustion of the element or its compounds, but the principal commercial source of this compound is the dust of copper, lead, and gold smelters. Most of the compounds of arsenic are produced from this oxide. It may be obtained in three allotropic forms of which one is amorphous and two are crystalline. It has

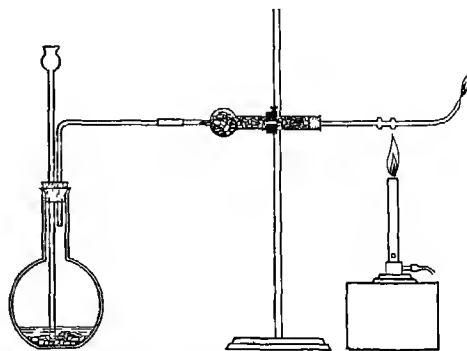


Figure 236 Diagram of Apparatus Used in the Marsh Test for Arsenic

a sweet taste and is extremely poisonous. It is used chiefly in the preparation of insecticides for spraying fruit trees and vegetables, for use in animal dips, for killing the boll weevil in cotton fields, and so on. It is also used to preserve furs, stuffed birds and animals, and skins. Certain compounds made from it are used as poisons for rats, flies, and ants, as preservatives for wood; as mordants in dyeing, and as weed-killers. Some is also used in decolorizing glass and in making enamels and opaque glass. Various compounds made from it are used in medicine, the best known of these compounds is *salvarsan*, used in the treatment of syphilis. Persons called upon to make unusual exertions sometimes take doses of arsenic trioxide to increase their endurance, mountaineers are said to use arsenic oxide for this purpose. The dosage may be increased gradually until the quantity taken at one time would be fatal to a person unaccustomed to its use. The trioxide is slightly soluble in cold water and more readily soluble at higher temperatures.

Arsenic oxide, commonly called the pentoxide, As_2O_5 , cannot be produced by burning arsenic in an excess of air. It is made by heating arsenic acid, of which it is the anhydride, until the water is expelled.



27. Acids and Their Salts

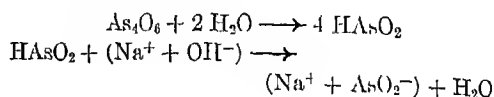
A solution of arsenic trioxide in water contains, probably, three very weak acids. These correspond to the formulas H_3AsO_3 (orthoarsenious), $\text{H}_4\text{As}_2\text{O}_5$ (pyroarsenious), and HASO_2 (metaarsenious). None of these has been produced in the pure state. However, salts of all of these acids have been prepared. The sodium or potassium salts correspond to the meta form of the acid and are, therefore, metaarsenites (KAsO_2 and NaAsO_2). The heavy metals form orthoarsenites, such as $\text{Pb}_3(\text{AsO}_3)_2$, Ag_3AsO_3 , etc. The most important salts of arsenious acid are those of copper

Scheele's green (CuHAsO_3)

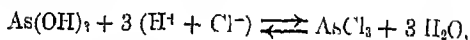
Paris green ($\text{Cu}_4(\text{C}_2\text{H}_3\text{O}_2)_2 (\text{AsO}_3)_2$)

These compounds are used as pigments and as insecticides.

Arsenic can be classified as an almost strictly acid-forming element, although arsenic trioxide, with the compound that it forms with water — arsenious acid or hydroxide — acts to a very slight extent as a base as well as an acid (page 520). Thus the oxide reacts with sodium hydroxide to form sodium arsenite, NaAsO_2 , which is a salt of metaarsenious acid.



The trioxide also dissolves in concentrated hydrochloric acid, possibly forming arsenic trichloride, AsCl_3 , and water. At least, the solution made in this manner contains some As^{+3} ions as indicated by the fact that hydrogen sulfide precipitates arsenic trisulfide, As_2S_3 , from it. The reaction with the acid,



is easily reversed, however, and arsenic trichloride is almost completely hydrolyzed in solutions that do not contain a high concentration of acid.

Arsenious acid and the trioxide are reducing agents and are oxidized by vigorous oxidizing agents to arsenic acid. When concentrated nitric acid acts upon the trioxide, and the solution is evaporated, crystals of $2 \text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ separate. Salts corresponding to the ortho-, pyro-, and metaarsenic acids are known. Calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, and the lead salts, $\text{Pb}_3(\text{AsO}_4)_2$ and PbHAsO_4 , are the most important of these salts; they are used as insecticides.

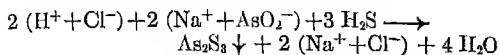
Arsenic acid and its anhydride act as oxidizing agents and are fairly easily reduced, this is one of the principal differences to be noted in comparing the compounds of arsenic and phosphorus.

Arsenic acid is a much stronger acid than arsenious acid and does not show as much tendency to react as a base with strong acids. Two of the tests for arsenate ion depend

upon the formation (1) of yellow powdery ammonium arsenomolybdate, $(\text{NH}_4)_3\text{AsO}_4 \cdot 12 \text{MoO}_3$, and (2) of white crystalline magnesium ammonium arsenate, $\text{MgNH}_4\text{AsO}_4$.

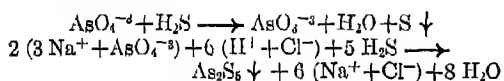
28. Sulfides

In solutions containing hydrochloric acid, compounds of trivalent arsenic react with hydrogen sulfide to form a precipitate of yellow arsenic trisulfide, As_2S_3

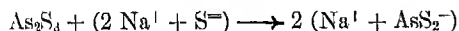
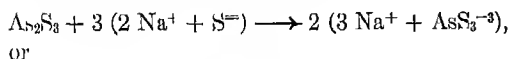


The hydrochloric acid prevents arsenic trisulfide from forming the colloidal state, which would remain dispersed in the solution instead of precipitating

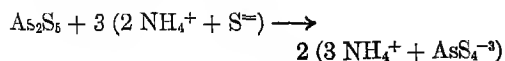
The pentasulfide, As_2S_5 , is precipitated by hydrogen sulfide from a solution containing the arsenate ion and an acid, usually hydrochloric acid. Some trisulfide is usually formed at the same time, because some of the arsenate ion is reduced to arsenite by hydrogen sulfide



The sulfides of arsenic are somewhat similar in chemical behavior to the oxides. The oxides react as acid anhydrides with sodium hydroxide, or similar bases, to form salts such as Na_3AsO_4 and $(\text{NH}_4)_3\text{AsO}_4$. The sulfides also possess acid properties and react with the sulfides of certain metals and with ammonium sulfide to form *thio-salts*. Thus, As_2S_3 reacts with sodium sulfide to form soluble sodium *thioarsenite*

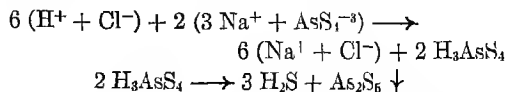


This salt resembles sodium arsenite, except that sulfur replaces oxygen. When ammonium sulfide is used as the basic sulfide, ammonium thioarsenite is produced. The pentasulfide reacts with these basic sulfides to form *thioarsenates*, which are water-soluble



When solutions of the thio salts are acidified, the

corresponding thio acids (H_3AsS_3 and H_3AsS_4) are probably first produced, but these decompose immediately into the sulfides and hydrogen sulfide



The trisulfide is oxidized to the pentasulfide if it is heated with polysulfides, such as Na_2S_2 or $(\text{NH}_4)_2\text{S}_x$ (page 497). These reactions are used in analytical chemistry to separate the sulfide of arsenic from other sulfides that are not acid in character and which do not react with sodium or ammonium sulfide to form soluble thio salts

ANTIMONY

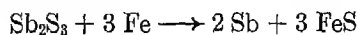
Antimony has been used, both as a metal and as certain of its compounds, since at least 2000 B.C. The metal was sometimes used in making vases and ornaments. The sulfide was used as a pigment and in cosmetics. Compounds of antimony were also used in medicine. Basil Valentine (fourteenth century) collected all that the alchemists knew about this element in his "Tiumphal Chariot of Antimony."

29. Occurrence

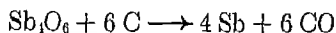
The principal ore of antimony is stibnite, Sb_2S_3 . The element also occurs in the free state. The world's annual production is about 30,000 tons, of which China normally produces about three fourths. In the United States, the production of antimony is limited to the recovery of the metal from scrap and used alloys, although deposits of antimony in the western states have been reported recently.

30. Production

The ore, stibnite, melts when heated to about 600°. In the liquid state, the antimony sulfide is separated from the rock and other earthy material of the ore and is then heated with iron



The liquid metal is heavier than the ferrous sulfide, which is also molten; the latter floats on top and can thus be drawn off. The sulfide can also be oxidized to the oxide by roasting in air, the oxide is then reduced with carbon



Electrolytic methods are also used in preparing the element.

31 Properties

Antimony is much more metallic in appearance and in properties than either phosphorus or arsenic. It has a silver-white, brilliant luster, is very brittle; has a specific gravity of 6.7, melts at 630° , is a poor conductor of electricity, and crystallizes from the molten state, with a slight expansion, to give a mass of rather large, beautiful crystals.

Antimony combines directly with the halogens, phosphorus, oxygen, and sulfur. It does not displace hydrogen from HCl, but it reacts with nitric acid to form the trioxide, which is slightly soluble in an excess of the acid. The failure of the metal and especially of its oxides to react with acids indicates that they have no pronounced base-forming properties, if the oxides were even moderately basic in character, they would react with the acid to form the nitrate of antimony. Antimony combines more slowly and less readily with oxygen than arsenic does, to form the oxides Sb_2O_3 and Sb_2O_5 . There are few well-established compounds that correspond to the latter oxide.

The trioxide of antimony is more typically amphoteric (page 525) than arsenic trioxide. Its behavior as an acid anhydride is shown by the salt, NaSbO_3 , that it forms when it reacts with sodium hydroxide. In this and in similar salts antimony plays the rôle of a non-metal. There are also salts, such as SbCl_3 and $\text{Sb}_2(\text{SO}_4)_3$, which are derived from the hydroxide, $\text{Sb}(\text{OH})_3$, and in which antimony acts as a trivalent metal. These salts, and sodium antimonite (NaSbO_2) as well, are strongly hydrolyzed in aqueous solutions;

this behavior indicates that the hydroxide, $\text{Sb}(\text{OH})_3$, formed by hydrolysis is only very slightly ionized either as the hydroxide-base or as the acid H_3SbO_3 or HSbO_2 , it is very weak both as a base and as an acid.

32 Uses

More than one half of the antimony used in the United States is consumed in the manufacture of bearing metal and storage battery plates for the automobile industry. Lead containing about 10 per cent of antimony is much harder than ordinary lead and is used in making such products as bullets and bearings. Antimonial lead is also resistant to the action of acids. Because it tends to expand when it solidifies, an alloy containing from 15–30 per cent of antimony is used as type metal. The expansion of the metal gives a sharp outline and a clear, distinct imprint of the type. Some kinds of pewter are alloys of antimony with tin and lead. Babbitt metal, which is used as an antifriction metal, is an alloy of antimony with tin and copper, it consists of hard crystals of antimony embedded in a softer matrix. Britannia metal is an alloy of similar composition. An alloy of antimony is used as a coating for copper telephone cables.

33 Stibine

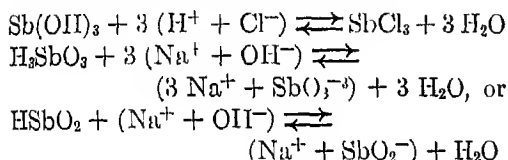
Stibine (SbH_3) is produced by the action of atomic hydrogen upon compounds of antimony. It is a poisonous gas and is closely related to arsine but is less stable. When the Marsh test is used for the detection of arsenic, antimony compounds, if present, produce stibine, which acts exactly as does arsine, and deposits a mirror of antimony when heated. The presence of arsenic must be confirmed by additional tests. The deposit of antimony is usually a more sooty-black than that of arsenic. It is also insoluble in reagents which dissolve the arsenic mirror, sodium hypochlorite and bleaching powder are used for this purpose. The antimony deposit also reacts with ammonium

polysulfide to give an orange precipitate of the sulfide, arsenic forms a yellow sulfide

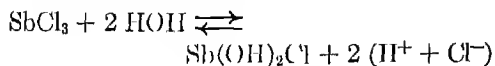
34. Other Compounds

The trioxide (Sb_2O_3) forms when antimony burns in oxygen or in air. Some Sb_2O_4 is formed at the same time. The pentoxide (Sb_2O_5) is formed by heating antimonie acid until the water which it contains is expelled. The tetroxide (Sb_2O_4) is formed when the trioxide is heated for some time in an excess of oxygen and below the temperature required for combustion. The trioxide and pentoxide are acidic oxides, and the trioxide shows some basic properties in forming salts with acids. The tetroxide is acidic, dissolving in alkalis to form hypoantimonates.

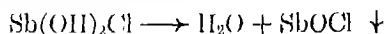
The amphoteric character of $\text{Sb}(\text{OH})_3$ is shown by the following reactions



This substance is very weak, both as an acid and as a base, as shown by the fact that both types of salts (SbCl_3 and NaSbO_2) are strongly hydrolyzed. Sodium antimonite (NaSbO_2), for example, reacts readily with water to form a solution of sodium hydroxide and antimonous acid, because the latter is very slightly ionized. The chloride hydrolyzes to form the basic chloride



The basic chloride then decomposes to give antimony oxychloride



Antimony trisulfide is an orange-red colored compound which precipitates when hydrogen sulfide is passed into a solution of the trichloride or slightly acidified solutions of antimonites and other compounds of trivalent antimony. The pentasulfide, Sb_2S_5 ,

is formed in a similar manner from compounds of pentavalent antimony. Like the sulfides of arsenic, both sulfides of antimony dissolve in solutions of the alkali or ammonium sulfides and polysulfides, forming thioantimonites and thioantimonates. Thus, with ammonium sulfide, $(\text{NH}_4)_3\text{SbS}_3$ and $(\text{NH}_4)_5\text{SbS}_4$ are formed from Sb_2S_3 and Sb_2S_5 , respectively. If ammonium polysulfide is used, the trisulfide is oxidized to the pentasulfide, which then reacts to form ammonium thioantimonate. When solutions containing the thio salts are acidified, antimony trisulfide is precipitated. The mineral form of antimony sulfide (stibnite) is black. The trisulfide is used in manufacturing red rubber and matches.

The precipitation of Sb_2S_3 from a solution containing an antimony compound shows that this element does exist, to some extent, as a cation in this solution. When the hydroxide acts as a base it sometimes appears to lose a molecule of water, forming the monohydroxide



The oxychloride (SbOCl) is a salt of this base, as is *tartar emetic*, $\text{KSbOC}_4\text{H}_4\text{O}_6$. The latter compound shows the SbO (antimonyl) radical replacing one hydrogen atom in tartaric acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$). Tartar emetic is used in medicine and as a mordant in dyeing.

BISMUTH

Bismuth was known as early as the fifteenth century, although it was often confused with antimony, tin, and lead. Not until about 1740 was it identified as a distinct substance, and its properties determined.

35. Occurrence

Bismuth occurs free in nature, and it is in this form that it is most often found. It also occurs as the oxide ($\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$) called *bismute*, and the sulfide (Bi_2S_3) called *bis-*

muthenate Some bismuth is produced in the United States as a by-product of lead smelters and refineries. The chief sources of the element and its compounds are found in the United States, Bolivia, Canada, and Spain. The metal is recovered from ores containing free bismuth by melting and separating the molten metal from the earthy portion of the ore. The sulfide ore is roasted to form the oxide, which is then reduced by means of carbon. The normal annual production is about 2000 tons from all sources.

3.6 Properties

Bismuth is a silvery gray metal with a reddish tint. It occurs in one form only: this is crystalline, lustrous, hard, and brittle. Its specific gravity is 9.8, it melts at 270°, and boils at 1450°.

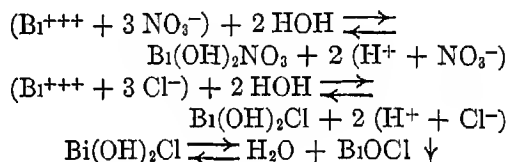
Bismuth burns to form the oxide Bi_2O_3 , but at low temperatures it reacts with oxygen very slowly and forms only a thin coat of oxide, which protects the metal from further oxidation. It combines directly, but not very vigorously, with the halogens, and also combines with sulfur. It dissolves readily in nitric acid to form the nitrate ($\text{Bi}(\text{NO}_3)_3$). This behavior is different from that of the other elements of this family. Antimony, for example, reacts with nitric acid to form first the oxide, which upon heating and further treatment with nitric acid gives antimonic acid, H_3SbO_4 . The formation of the nitrate by bismuth shows its definitely metallic character in contrast to the non-metallic nature of the other members of its family. The element also dissolves in concentrated sulfuric acid, in much the same manner that copper does, to form the sulfate ($\text{Bi}_2(\text{SO}_4)_3$). It slowly dissolves in hydrochloric acid, in the presence of air, to form the chloride (BiCl_3).

3.7. Compounds

In practically all its compounds, bismuth acts as a trivalent metal, forming simple salts such as BiCl_3 and $\text{Bi}(\text{NO}_3)_3$. Its hy-

dride, *bismuthine* (BiH_3), is an extremely unstable compound and very little is known about it. It has none of the basic properties possessed by ammonia. The most familiar oxide is Bi_2O_3 , which forms when the metal is heated in the air. The monoxide BiO is prepared by heating basic bismuth oxalate ($\text{BiO})_2(\text{C}_2\text{O}_4)$, and the pentoxide, Bi_2O_5 , is formed by the action of vigorous oxidizing agents upon the trioxide.

The trioxide is a yellow solid. It does not react with bases and therefore has no acid properties. It dissolves in acids, and when the solutions are evaporated, normal salts — such as the chloride, nitrate, or sulfate — are obtained as crystals. These salts hydrolyze readily, when water is added, to form basic salts.



Bismuth oxychloride may be regarded as a salt of the base, *bismuthyl hydroxide*, $\text{BiO}(\text{OH})$. The oxychloride is known as *pearl white* and is used as a white paint pigment and in face powders. The basic nitrate is best known as *bismuth subnitrate*. The commercial preparation, which contains some bismuthyl hydroxide, is used medicinally as an antacid in treating digestive troubles, and in the treatment of ulcers and skin diseases. The subcarbonate of bismuth, $(\text{BiO})_2\text{CO}_3$, is used for similar purposes. The addition of sodium, potassium, or ammonium hydroxide to the solution of a bismuth salt causes the precipitation of the hydroxide, $\text{Bi}(\text{OH})_3$. Unlike the corresponding hydroxide of antimony ($\text{Sb}(\text{OH})_3$), this compound is not amphoteric, and consequently does not dissolve in an excess of the base.

The pentoxide is relatively inactive. It does react, however, with very concentrated solutions of sodium hydroxide to form sodium bismuthate, NaBiO_4 , which hydrolyzes

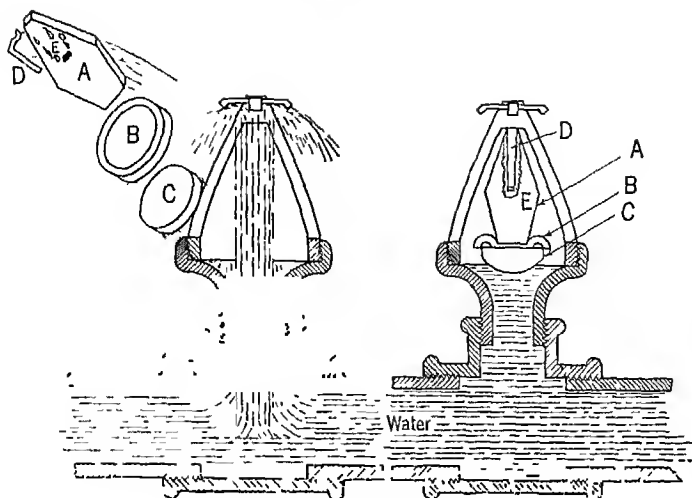


Figure 237 Automatic Sprinkler

D is made of the low-melting alloy solder, it holds the strut composed of A, B, and C in place. When D melts, the pressure of the water throws A, B, and C out of the way, and the water escapes through the opened valve.

in water, or reacts when an acid is added, to form the very weak acid, HBiO_3 . This acid and its salts correspond to nitric acid and the nitrates, and show that, in its highest valence state, bismuth possesses, to a slight degree, the non-metallic and acid-forming properties of the other members of the family. Bismuthic acid is a very powerful oxidizing agent. It is used in analytical chemistry in detecting and estimating manganese. It oxidizes manganous (Mn^{+2}) ion to permanganate (MnO_4^-) ion.

Bismuth trisulfide, Bi_2S_3 , is precipitated as a brown compound when hydrogen sulfide is passed into a solution containing a bismuth salt. Like the trioxide, it has no acid properties and consequently does not dissolve in solutions of sodium or ammonium sulfide to form thio salts. Advantage is taken of this difference in behavior in separating bismuth from arsenic and antimony in the analytical laboratory.

38 Uses of Metallic Bismuth

Metallic bismuth is used in the preparation of many alloys. The presence of bismuth in these alloys gives low melting points and prevents shrinkage upon solidification, since bismuth expands upon cooling. Ex-

amples of these alloys and their composition are given below.

	Bi	Pb	Sn (Parts)	Cd	Melting Point
Wood's metal	50	25	12.5	12.5	71°
Rose's metal	50	25	25		94°

These low-melting alloys are used for many purposes: electrical fuses, automatic fire alarms, automatic sprinkler systems, releases on automatic fire doors, and safety plugs for boilers. Most of these applications are of value in the prevention and control of fires. When slightly heated, the bismuth alloy melts, releasing water from the sprinkling systems, closing an electrical circuit which rings a bell; or automatically removing the stops that hold open fire doors. Bismuth alloys are also used as anti-friction metals to some extent.

Review Exercises

1. Summarize in tabular form the properties of the elements of the nitrogen family. Point out the changes in the properties of the elements from nitrogen to bismuth. The summary should include typical compounds of the elements as well as the elements themselves. The following compounds should be considered: hydrides, chlorides, oxides, acids, bases, typical salts, and sulfides.

2. If a sample of rock phosphate contains 80 per cent of $\text{Ca}_3(\text{PO}_4)_2$, how much of this material would be required for the production of one ton of superphosphate (including the calcium sulfate produced)? Consider superphosphate as $\text{Ca}(\text{H}_2\text{PO}_4)_2$.
3. What weight of (1) phosphorus and (2) phosphoric acid could be produced from the weight of rock phosphate calculated above?
4. Show why a solution of primary sodium phosphate is slightly acid, whereas a solution of secondary sodium phosphate is alkaline.
5. Which should have a higher pH, a solution of primary sodium phosphate or primary ammonium phosphate? Explain.
6. Starting with rock phosphate, outline a series of reactions which could be used to prepare the salt Na_3PO_3 .
7. How would you proceed to bring about the transformations indicated below? $\text{Sb}_2\text{S}_3 \rightarrow \text{Sb}$, $\text{Sb} \rightarrow \text{SbOCl}$, $\text{Na}_2\text{HPO}_4 \rightarrow \text{Na}_4\text{P}_2\text{O}_7$, $\text{Bi} \rightarrow \text{Bi}_2(\text{SO}_4)_3$, $\text{As} \rightarrow \text{H}_3\text{AsO}_4$, $\text{Ca}_3(\text{PO}_4)_2 \rightarrow \text{H}_3\text{PO}_4$, $\text{Ca}_3\text{P}_2 \rightarrow \text{PH}_3$, $\text{NaAsO}_2 \rightarrow \text{As}_2\text{S}_3$.
8. Explain the meaning of the term *amphoteric hydroxide*. What hydroxides of the members of this family are amphoteric and which are not? Illustrate the behavior of one of the hydroxides that is amphoteric and one that is not amphoteric.
9. Suggest two methods of separating bismuth from arsenic, starting with a solution which contains BiCl_3 and NaAsO_2 . Write equations for all necessary reactions.
10. Identify arsine, bismuth subnitrate, Wood's metal, tertiary sodium phosphate, meta-arsenic acid, bismuth oxychloride, bismuthic acid, Marsh's test, Paris green, white arsenic, ammonium thioarsenite, and arsenopyrite.
11. Show the relationships between the three phosphoric acids and their anhydride.
12. Write equations for the following reactions:
 - (1) $\text{BiCl}_3 + \text{NaOH} \rightarrow$
 - (2) $\text{Na}_2\text{HPO}_4 + \text{CuCl}_2 \rightarrow$
 - (3) $\text{P} + \text{HNO}_3 \rightarrow$
 - (4) $\text{BiOCl} + \text{H}_2\text{S} \rightarrow$
 - (5) $\text{Ca}_3(\text{PO}_4)_2 + \text{SiO}_2 + \text{C} \rightarrow$
 - (6) $\text{Na}_2\text{HPO}_4 \xrightarrow{\text{heat}}$
 - (7) $\text{H}_3\text{AsO}_3 + (\text{H}) \rightarrow$
 - (8) $\text{Na}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow$
13. Write an equation for the reaction between arsenic trisulfide and sodium sulfide, Na_2S . Show that this reaction is similar to that which occurs when As_4O_6 dissolves in a solution of NaOH .
14. Account for the natural occurrence of bismuth and antimony in the free state. Why is phosphorus not found in the free state?
15. Given a sample which may be phosphorus, bismuth, arsenic, or antimony. What physical appearances or properties would you look for as means of distinction? How would you proceed by chemical methods to determine which of the elements is present, assuming that the sample contains only one of the four?
16. Why is antimony sulfide not hydrolyzed in the same manner as antimony chloride?
17. In using the Marsh test, the mirror of arsenic produced in the tube of the apparatus weighed 10 mg. The material tested weighed 10 g and contained As_4O_6 . What weight of As_2O_3 was present per 100 g of the material tested?
18. What reactions can be used to produce the following changes in the order indicated: $\text{As}_4\text{O}_6 \rightarrow \text{As}_2\text{S}_3 \rightarrow \text{Na}_3\text{AsS}_3 \rightarrow \text{As}_2\text{S}_3$?
19. Starting with 10 g of As_4O_6 , what weight of As_2S_3 should one obtain by the series of reactions in 18, assuming that there are no losses?
20. What weight of primary sodium phosphate can be produced from the phosphoric acid made by the oxidation of 10 g of phosphorus with nitric acid?
21. To one liter of 0.1 N solution of orthophosphoric acid, sufficient calcium chloride is added to precipitate the phosphate ion completely. What weight of $\text{Ca}_3(\text{PO}_4)_2$ can be produced by this procedure?
22. Name the compounds corresponding to the following formulas: NaBiO_3 , SbOCl , NaSbO_3 , $(\text{NH}_4)_3\text{AsS}_4$, $\text{Pb}_3(\text{AsO}_4)_2$, CaH_2PO_4 , K_2HPO_4 , NaPO_3 , $\text{H}_4\text{P}_2\text{O}_7$, and Ca_3P_2 .

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SILICON AND RELATED ELEMENTS

That silica or siliceous earth is composed of a combustible body united with oxygen, was demonstrated by Sir H. Davy. To this substance, on the supposition of its being a metal, the term silicium was applied.

CHEMISTRY TEXT OF 1828

1 Introduction

The family to which silicon belongs is in group four of the periodic classification and includes carbon, titanium, zirconium, and hafnium. These elements are acid forming (non-metallic) in character, although metallic and base-forming properties increase with increasing atomic weights as in other families. Boron of group three is the only element of that group that does not show decided metallic properties. In some respects the element and its compounds resemble silicon and its compounds, the principal compounds of both elements, for example, are those in which the elements appear in negative radicals or ions, such as SiO_3^- and BO_3^- . For these reasons the chemistry of boron is discussed in this chapter.

SILICON

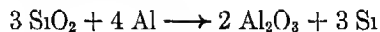
2 Occurrence

Silicon does not occur in nature as the free element. Its compounds, however, are very abundant, forming about 87 per cent of the solid crust of the earth. The element is second only to oxygen among the constituents of the outer portion of the earth, which contains about 26 per cent of silicon. Among minerals, including rocks and soils of all kinds, silicon plays the fundamental rôle, just as carbon does in the compounds associated with organic matter.

One of the most abundant compounds of silicon is the oxide called silica, SiO_2 . This occurs most abundantly in sand and in sandstone. It also occurs in many crystalline forms including several varieties of quartz — *rose quartz*, *amethyst*, *milky quartz*, and *rock crystal* — and chalcedony, carnelian, onyx, agate, flint, jasper, and opal (page 532). Other minerals containing silicates of different kinds include granite, shale, clay, marl, micas, feldspars, asbestos, tourmaline, topaz, and many others. These are discussed at greater length on page 532.

3. Preparation of the Element

Small samples of silicon can be prepared by reducing silica by means of powdered aluminum or magnesium.



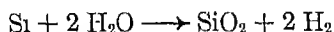
The mixture must be strongly heated. The aluminum melts and dissolves the silicon as it is formed. As the solution cools, the silicon separates as metal-like crystals, and the aluminum is removed by dissolution in an acid. The element is also prepared by reducing its chloride, SiCl_4 , with metallic sodium. Commercially, silicon is now produced by reducing the oxide with carbon in an electric furnace. Some difficulty is encountered in preventing the silicon and carbon from reacting to form a carbide, but a product containing 98 per cent of silicon is

made by this reaction. If a mixture of silica and the oxide (Fe_2O_3) of iron is reduced by carbon, an alloy of iron and silicon, called *ferrosilicon*, is produced. Since the principal use of silicon is in the preparation of steels of special properties, ferrosilicon, instead of pure silicon, is often produced

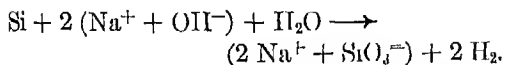
4. Properties

Like carbon, silicon has a crystalline form, and also what is often called an amorphous form. The latter is a brown powder that really consists of very small crystals. Crystalline silicon has a structure resembling that of diamond. It is hard enough to scratch glass, has a density of 2.4, melts at 1420° , boils at 2600° , and is a fair conductor of electricity. Crystalline silicon is less active in chemical reactions than the amorphous form.

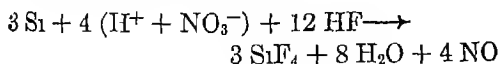
The element reacts readily with the halogens to form SiF_4 , SiCl_4 , SiBr_4 , and SiI_4 . With fluorine the element reacts spontaneously and is ignited by the heat liberated in the reaction. Amorphous silicon combines with iodine only when the mixture of the elements is heated to a red heat. Silicon burns when heated in the presence of oxygen, but combustion is retarded by the formation of a coat of the oxide that forms on the surface. It reacts slowly with steam to liberate hydrogen



It dissolves readily in sodium hydroxide, forming sodium silicate and hydrogen (page 110)



It dissolves in a mixture of HNO_3 and HF , but not in HCl or H_2SO_4



When heated, it also reacts with sulfur (SiS_2), carbon (SiC), nitrogen (Si_3N_4), and many metals. The compounds with the metals are

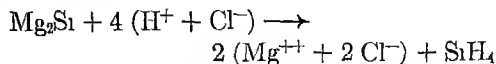
called *silicides*. Typical silicides are Li_3Si , Mg_2Si , FeSi (ferrosilicon), and CoSi_3

5. Uses

Although one of the most abundant of the elements, silicon in its free state has few uses. It is an essential, however, in the steel industry. Ferrosilicon is added during the production of steel as a deoxidizing agent to remove dissolved oxygen, which weakens the finished product. It also removes the iron carbide, Fe_3C , in iron and thus produces a soft, gray iron instead of a harder, white product. Silicon steel contains up to 5 per cent of silicon. This variety of steel has desirable magnetic properties and is used in making the cores of transformers and electromagnets. If 15–16 per cent of silicon is added, the steel is very hard and resistant to corrosion and the attack of acids. *Duriron* and *Tantiron* are alloy steels of this kind. The steel used in making springs contains manganese and silicon. An alloy of aluminum and silicon is used in automobile manufacture. Uses of silicon compounds will be mentioned as these compounds are discussed

6. Hydrides

Silicon forms several compounds with hydrogen. These are SiH_4 , Si_2H_6 , Si_3H_8 , Si_4H_{10} , $\text{Si}_n\text{H}_{2n+2}$. They are analogous to certain hydrogen-carbon compounds. Several of these, particularly SiH_4 , are formed when magnesium silicide is treated with dilute HCl



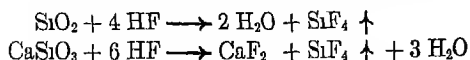
The hydrides ignite spontaneously in the air and react with cold water to form silicon dioxide and hydrogen

7. Halides

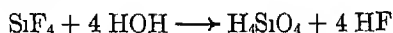
The halides of silicon have the general formula SiX_4 . They can be prepared by the direct combination of silicon and the halogens, but the combination is less readily ac-

complished as the atomic weight of the halogen increases

Silicon tetrafluoride (SiF_4) is not prepared by direct combination, because of the difficulty of obtaining free fluorine and free silicon. It is usually made by allowing hydrofluoric acid to act upon silica or a silicate



It is a colorless, non-combustible gas, which fumes in moist air. With water it hydrolyzes as follows

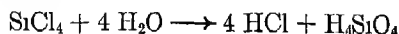


A part of the silicic acid precipitates as H_4SiO_4 or H_2SiO_3 . $\text{H}_4\text{SiO}_4 \longrightarrow \text{H}_2\text{O} + \text{H}_2\text{SiO}_3$. A part reacts with more hydrofluoric acid to form *fluosilicic acid*



Fluosilicic acid is a moderately strong electrolyte. It is sometimes used to detect potassium ion in the presence of sodium ion, since K_2SiF_6 is not very soluble while Na_2SiF_6 dissolves readily.

Silicon tetrachloride (SiCl_4) is produced when chlorine is passed over a heated mixture of silica and carbon. It is also made by the action of chlorine upon the carbide of silicon. The chloride hydrolyzes completely. When it comes into contact with moist air it fumes strongly, producing a dense smoke-cloud which consists of droplets of hydrochloric acid solution and small particles of silicic acid



If ammonia is present, it reacts with the hydrogen chloride and produces a still denser smoke. Mixtures of this kind are used to make smoke screens. Titanium tetrachloride is similarly used.

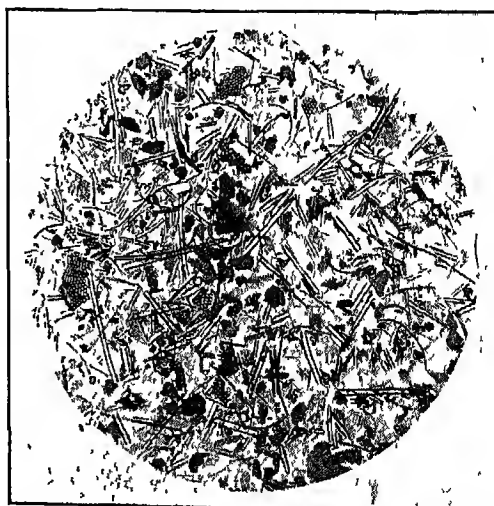
8. Silicon Dioxide

Silicon forms two oxides, the monoxide, SiO , and the dioxide, SiO_2 . The former is

made by reducing the dioxide with carbon under controlled conditions. It has a yellowish-brown color and is relatively unimportant.

The dioxide, commonly called silica, occurs in nature in many forms. Silicon occurs chiefly as silica or in the silicates which are derivatives of this oxide. Pure silica occurs as beautiful, colorless crystals of *quartz*, which is also called *rock crystal*. The rock crystals belong to the hexagonal system and are of two different varieties, "right-handed" and "left-handed". One of these bears the same relation to the other as an object bears to its image in a mirror. The crystals grow to enormous size in nature, some of those which are found weigh several hundred pounds. Small amounts of impurities are sometimes present, and these give crystals of characteristic colors. The *amethyst* is quartz plus a trace of an oxide of manganese. Small air bubbles are responsible for the appearance of *milky quartz*. Rose quartz, onyx, jasper, agate, flint, opal, petrified wood, and chalcedony are other forms of impure silica. The dioxide is also present in granite and in gneiss, and constitutes most of the material in sand and sandstone.

Some silica is present in a few forms of



Courtesy of Johns-Manville Company

Figure 238. Diatomaceous Earth, Magnification 380 X

animal and plant life, such as bamboo, rushes, straw, feathers of certain birds, and sponges. Small organisms that live in water, called diatoms, have skeletons of silica. Collections of these skeletons form deposits of diatomaceous earth or *kieselguhr*. This material is porous and very adsorbent; hence, it is widely used to adsorb colored substances from oils and other liquids. It is also used in soaps and in metal polishes as a mild scouring powder.

When quartz is heated to about 870° , it changes into the crystalline form known as *tridymite*, and at 1450° the latter changes into a third crystalline modification, called *cristobalite*. When heated to temperatures above 1700° , quartz gradually softens, and eventually forms a thick liquid. This is somewhat like glass and can be used to make beakers, tubing, crucibles, flasks, and other laboratory articles. Vessels made of fused quartz are expensive but have many desirable properties, because of the small coefficient of expansion of quartz, they are not likely to break when heated and suddenly cooled. A beaker made of quartz can be heated to redness and then immersed in ice-water without breaking. Quartz also resists the chemical action of practically all reagents, except strongly alkaline solutions or fused alkalis, and is less soluble in water than glass.

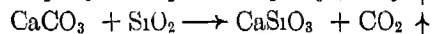
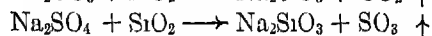
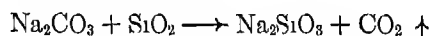
Quartz also allows ultraviolet light to pass through it, while ordinary glass does not. Since ultraviolet light rays are thought to have desirable physiological effects in the treatment of certain diseases, windows in the sun-rooms of hospitals are sometimes made of quartz instead of glass. The tubes in mercury vapor lamps — used to produce ultraviolet light — are also made of quartz.

If quartz is heated until it softens, bubbles of different gases, including air and water, make the quartz opaque. This is called vitreous quartz and is used to make many kinds of apparatus, particularly large quartz tubes and evaporating dishes. Clear quartz is made by reducing the pressure in the furnace in which it is melted. The decreased pressure causes most of the bubbles of gas to escape. A higher temperature makes the fused quartz more fluid and aids in the release of the bubbles. A high pressure is desirable as the quartz cools, since this tends to compress into

negligible volumes the bubbles that do not escape.

9 Chemical Properties of Silica

Silica does not dissolve in water, and since it has no basic properties it is also insoluble in acids (except hydrofluoric). It is the anhydride of silicic acid, and consequently reacts with (fused) alkalis, such as NaOH or KOH, to form silicates. Several acids and their salts are derivatives of this anhydride. When heated with certain oxygen salts, whose acid anhydrides are volatile, it forms silicates and releases the oxide of the non-metal of the salt.



These reactions are important in the manufacture of glass.

10 Silicic Acid

When a solution of sodium silicate is acidified, there is formed a gelatinous precipitate, which is commonly called silicic acid. A colloidal dispersion of this substance is produced if a solution of sodium silicate is mixed with a large excess of hydrochloric acid. The gelatinous precipitate is really hydrated silicon dioxide, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, in which the



Courtesy of Johns-Manville Company

Figure 239 Crude Asbestos Fiber Mined in Quebec

quantity of water combined with silica varies over a considerable range. Frequently, however, the hydrous oxide is called silicic acid and a definite formula is assigned to it largely as a matter of convenience. Because salts (silicates) corresponding to their formulas are known among mineral substances or have been prepared, several hypothetical silicic acids are frequently mentioned in the literature of chemistry.

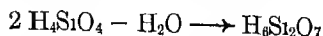
Orthosilicic acid is H_4SiO_4 . Many minerals are salts of this hypothetical acid. Some of these are

Mica	$\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$
Willemite	Zn_2SiO_4
Zircon	ZrSiO_4
Foisterite	Mg_3SiO_4
Pyrope	$\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$
Andalusite	$(\text{AlO})\text{AlSiO}_4$

Metasilicic Acid, H_2SiO_3 , is the hypothetical acid corresponding to many other natural silicates, among which are

Chrysocolla	$\text{CuSiO}_3 \cdot 2 \text{H}_2\text{O}$
Wollastonite	CaSiO_3
Talc	$\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$
Beryl	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$
Asbestos	$\text{Mg}_3\text{Ca}(\text{SiO}_3)_4$

Other silicates correspond to the *polysilicic acids*. The hypothetical *disilicic acids*, $\text{H}_6\text{Si}_2\text{O}_7$, $\text{H}_4\text{Si}_2\text{O}_6$, and $\text{H}_2\text{Si}_2\text{O}_5$, are considered as the products resulting from the loss of one, two, and three molecules of water, respectively, by two molecules of orthosilicic acid. Such compounds are sometimes called *condensed acids*. For example



The *trisilicic acids* are formed in a similar manner by the loss of different numbers of molecules of water by three molecules of H_4SiO_4 . Some of the trisilicates found as minerals are

Orthoclase	KAlSi_3O_8
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}$
Albite	$\text{NaAlSi}_3\text{O}_8$

The colloidal state of silicic acid or hydrated silicon dioxide has the ability to adsorb certain ions from water solutions, and the adsorbed substances are not easily removed by water. This property of silicic acid, which is always present to some extent in soils, is responsible in part, for the retention by the soil of potassium salts and nitrates, both of which are essential to fertility. The retention of potassium by soils also depends upon the presence of zeolites, which are hydrated sodium-calcium-aluminum silicates. When water containing potassium salts in solution comes into contact with zeolites, the sodium which they contain is replaced by potassium, and sodium ion is released in the solution.

11 The Structure of the Silicates

The natural silicates are crystalline substances, and their crystal lattices are composed of metallic ions and different silicon-oxygen ions. Some contain the SiO_4^{4-} ion, Section 10. This ion has a tetrahedral structure (Figure 240) with a silicon atom at the center and four oxygen atoms at the corners of the tetrahedron. The metallic ions lie between adjacent tetrahedra, forming a pattern that resembles the lattice of sodium chloride.

The disilicate ion, $\text{Si}_2\text{O}_7^{6-}$, consists of two SiO_4^{4-} tetrahedra which share one atom of oxygen between them (Figure 241). In the trisilicate ion, $\text{Si}_3\text{O}_9^{6-}$, three tetrahedra are involved, each of which shares one atom of oxygen with each of the other two (Figure 242). The SiO_4^{4-} tetrahedra in other silicates, such as $\text{CaMg}_3(\text{SiO}_3)_4$, one of the forms of asbestos, are joined together

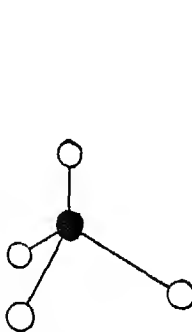


Figure 240 Tetrahedral Structure of the Silicate Ion

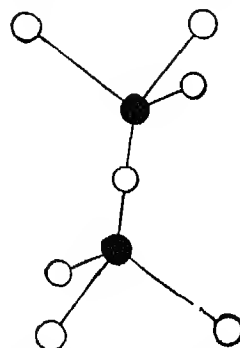


Figure 241 Disilicate Ion with Two Tetrahedra Sharing One Atom of Oxygen

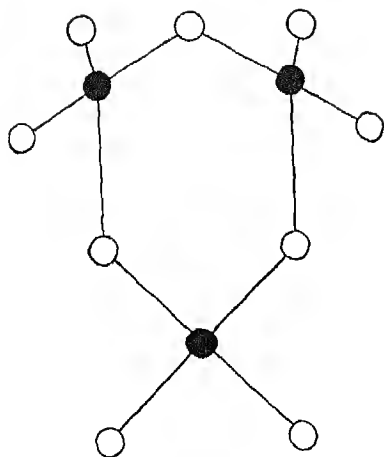


Figure 242 The Trisilicate Ion with Three Tetrahedra Each Sharing Two Oxygen Atoms

by sharing oxygen atoms to form long chains, with metallic ions tending to bind the chains together by electrostatic attraction (Figure 243). The micas consist of sheets containing tetrahedra that share oxygen atoms. The sheets are weakly held together by ions of the metals. Mica readily splits into thin sheets for this reason. In still other silicates, especially in the feldspars, the tetrahedra are joined to form a three-dimensional network, leaving open spaces in which the ions of the metals and sometimes molecules of water are held.

12 Silica Gel

When silicic acid jelly is dehydrated by heating at 300° under reduced pressure, until it contains only a small percentage of water, the product is called *silica gel*. This substance has excellent adsorbing properties for gases and the vapors of many substances. Some of the substances adsorbed are nitrogen, sulfur dioxide, benzene, nitrogen dioxide, and the vapors of practically all volatile organic liquids. The gel is heated, when it has adsorbed its full capacity, to release the adsorbed substances. Because of this property, silica gel serves as a contact catalyst in many reactions.

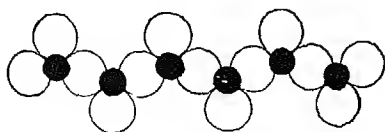


Figure 243

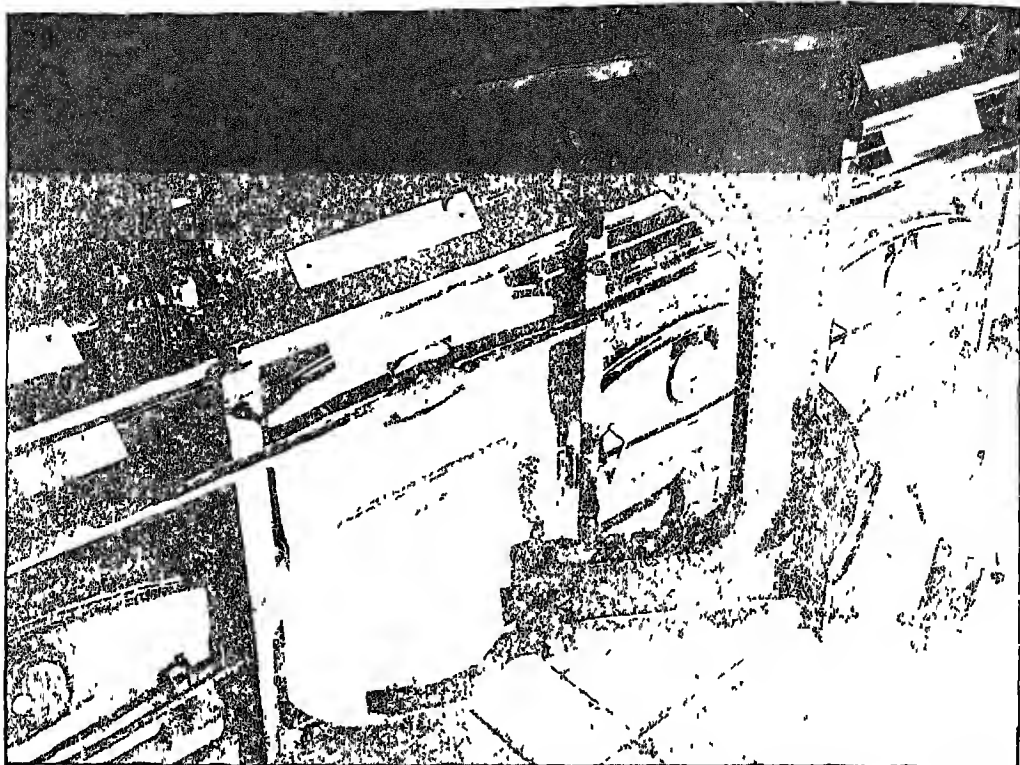
13 Sodium Silicate

Sodium silicate (Na_2SiO_3) is made by heating silica with sodium hydroxide or sodium carbonate (page 533). It is usually marketed as a concentrated, viscous solution and is commonly known as *water glass*. As the solution is heated, it becomes more viscous and finally gives a hard, glass-like mass. Since it is the salt of a strong base and a weak acid, sodium silicate hydrolyzes in water to give strongly alkaline solutions. Because of this property, it is used in some soaps and washing powders. It is also used as an adhesive in making boxes of pasteboard; in rendering materials fireproof, as a preservative of eggs, in the manufacture of cement and mortars, and as a coating on porous surfaces to make them waterproof.

14 Glass

Glass-making dates back to many centuries before the Christian Era. The Egyptians made and used glass at least as early as 1400 B.C. Glass is usually a mixture of silicates, but some of the silica may be replaced by the oxide of boron, B_2O_3 , or the oxides of certain other non-metallic elements. The metals in common, soft glass are sodium and calcium. The sodium may be replaced by potassium in hard glass, which does not soften until it has been heated to relatively high temperatures. The substitution of other materials produces glass of special properties. Ordinary soft glass is made by heating together sand, sodium carbonate or sodium sulfate, and calcium carbonate (page 533). The product is clear, brittle, and amorphous, it has no crystalline structure and, upon the basis of physical properties, is classified as a supercooled liquid. Old glass is frequently found to have developed a crystalline structure. When it is heated, glass softens gradually but has no definite melting point.

Melted glass, as it comes from the pots of the glass-making furnace, is worked into different articles by means of a blowpipe, or the objects are blown in molds by compressed



Courtesy of Libbey-Owens Ford Glass Company

Figure 244 Withdrawing a Pot of Molten Glass from Furnace

an The latter practice has largely replaced the glass blower. Glass for window panes is first made into long cylinders, or it is drawn out into flat ribbons. The cylinders are cracked and softened in a furnace until they flatten out to form sheets of glass, which are then rolled to the desired thickness. Plate glass is made by rolling a mass of softened glass. All articles made of glass must be *annealed* by passing them through a long, heated chamber or a furnace that has a high temperature at the entrance and a low temperature at the exit. Annealing prevents the formation of strains in the glass by rapid cooling.

Common glass is a mixture of sodium and calcium silicates with an excess of silica. (See equations, page 533.) This glass — commonly called soda glass — is used for window panes, bottles, dishes, and many other articles. It softens at a relatively low

temperature and is easily worked into different forms. The composition of different kinds of glass is shown in Table 31, in which the *approximate* percentages of the constituents are given.

Hard glass, which must be heated to a higher temperature than soda glass before it softens, is a potash glass. *Pyrax* brand is a sodium-aluminum borosilicate, in which there is an excess of silica. The lead-potash glasses are soft but have a high index of refraction and are very brilliant. The lead glasses are used as paste in making imitations of diamonds and other gems, lenses for optical instruments, and some cut glass articles. Jena glass, which at one time was imported into the United States in large quantities, is composed of zinc-barium borosilicates.

15 Color of Glass

Common glass is often slightly green in

TABLE 31

The Composition of Glass

Glass	SiO ₂	Na ₂ O	CaO	K ₂ O	PbO	B ₂ O ₃	As ₂ O ₃	Al ₂ O ₃
Soda Glass	75	15	8					2
Optical Glass	71	5	10	13			0.8	0.2
Pyrex Brand	80.6	3.8	0.4	0.6		11.3		2
Potash Glass	80	0.6	7	12				0.4
Lead Glass	55			11	33			1

color because of the presence of small amounts of ferrous silicate. This color is changed to the less noticeable yellow of ferric silicates by the addition of manganese dioxide as an oxidizing agent during the manufacture of the glass. Blue glass is made by adding cobalt to form cobalt silicate. Colloidal dispersions of copper and gold produce red or ruby glass. Selenium decolorizes green glass and is also used to make red glass. Violet glass contains manganese, and green glass, chromium or copper. Opaque or white glasses are produced by adding substances such as stannic oxide, calcium fluoride, and boric acid, which are suspended in the glass, or which melt without reacting with the other constituents.

16 Special Kinds of Glass

The non-shattering glass now used in automobiles and in bullet-proof windows is made by placing sheets of cellulose acetate between layers of sheet glass. Recently, inexpensive commercial glass that transmits ultraviolet light has been produced for use in hospitals and elsewhere as a substitute for quartz. A strong, flexible plate glass, which crumbles when it is broken, is made by suddenly cooling (tempering) the surface of plate glass in a stream of cold air.

Glass bricks are used in constructing walls of buildings, thus making windows unnecessary. This use of glass is important in air-conditioned buildings. Spun glass, or glass fibers, consists of filaments made by drawing

out softened glass through dies. These filaments can be woven into fabrics, which are used, for example, in making window curtains. Spun glass is also used as a means of heat insulation and as a filter for gases and liquids. Invisible glass can be produced by coating the surface with a thin layer of certain kinds of soaps or of sodium fluoride. Glass is visible because of the light that it reflects. The layer on the surface of invisible glass interferes with reflection.

17. Uses of Silicates

In addition to their use in the manufacture of glass, silica and silicates are essential raw materials in the cement industry and in the manufacture of brick, tile, porcelain, terra cotta, and other *ceramics*. Many of the natural silicates are used in large quantities for various purposes. Mica is used as an electric insulator, as a decorative material ("snow"), in paints, and in the windows of stoves. Asbestos is used as an insulating material around hot water, hot air, and steam pipes; in the manufacture of fireproof fabric, and with cement in the manufacture of fireproof shingles. Talc is used in "talcum powder," soap, paint, rubber, and paper. Soapstone is utilized for switchboards, table tops, and sinks; in composition it is much like talc. Manufactured zeolites (page 534) are used in softening water. Silica is used as a flux, as in the production of phosphorus from rock phosphate. It reacts with calcium oxide to form the easily fused calcium



Courtesy of Corning Glass Works

Figure 245 Fabrication of a Soxhlet Extractor

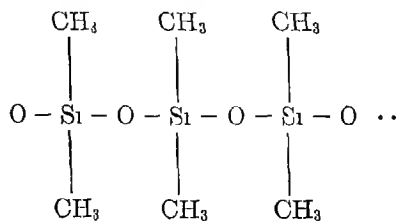
silicate (slag). Since it is the oxide of a non-metal, silica is an acid flux and is added when a basic material is to be converted into slag. Conversely, when silica is the impurity to be removed from an ore, a basic flux, such as calcium oxide, is added. This is usually provided in the form of calcium carbonate, which reacts with the silica to form calcium silicate and to liberate carbon dioxide.

Rock wool is made from certain natural silicates and from blast-furnace slag, which is largely composed of silicates. The silicate is fused and a thin stream of the liquid is subjected to a blast of steam, which breaks up the stream into drops. Under the pressure of the steam blast, the viscous liquid of each drop is forced out into a fine thread, which quickly solidifies. Masses of these threads make efficient insulation against loss of heat or, when placed in the walls and attics of houses,

protect the interiors in summer from the heat outside.

18 Silicones

These interesting compounds have recently received considerable attention. Their structures consist of SiO_2 groups linked together in the form of chains or rings. In addition to oxygen atoms, organic radicals, such as CH_3 or C_2H_5 , are also attached to the atoms of silicon. A simple silicone may be represented as follows:



The bonds that unite the different units of the chain are oxygen-silicon bonds (O-Si). There are several types of silicones. Those that have a chain structure are usually only liquids and are used as lubricants in airplane motors. Other silicones resemble rubber, resins and other plastic materials. They are used for electrical insulation on wire, as waterproof coatings on cotton and wood, and for several other purposes.

BORON

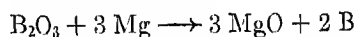
19 Occurrence

Boron is not an abundant element, it constitutes about 0.001 per cent of the earth's crust. It occurs as boric acid, H_3BO_3 , and as salts of condensed boric acids. The Stassfurt deposits contain magnesium borate.

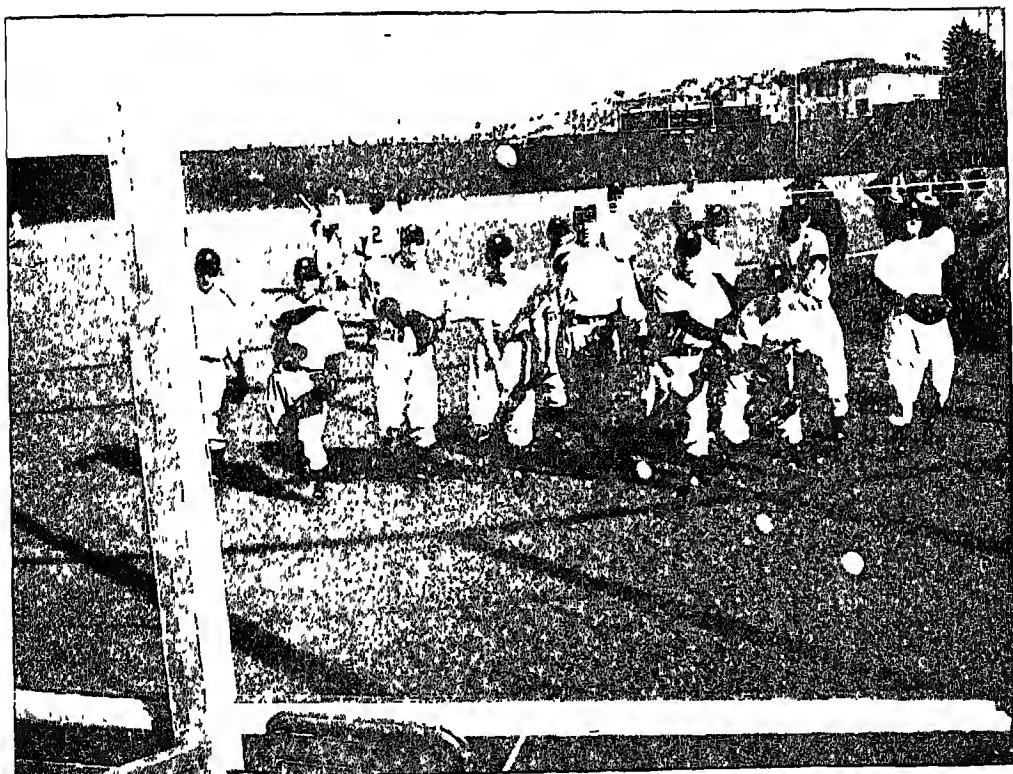
Deposits in Death Valley, California, contain *ulexite*, $NaCaB_5O_9 \cdot 8 H_2O$, *Colemanite* ($Ca_2B_6O_{11} \cdot 5 H_2O$), *rasorite* ($Na_2B_4O_7 \cdot 4 H_2O$), and *borax* ($Na_2B_4O_7 \cdot 10 H_2O$), are found in the Mohave Desert of California. Borax is also produced during the recovery of potassium compounds from Searles Lake (page 390). The total annual production in the United States is about 300,000 tons, this is approximately 95 per cent of the normal production of the world.

20. Preparation

Boron oxide is difficult to reduce, but the reduction can be accomplished by heating the oxide with magnesium.

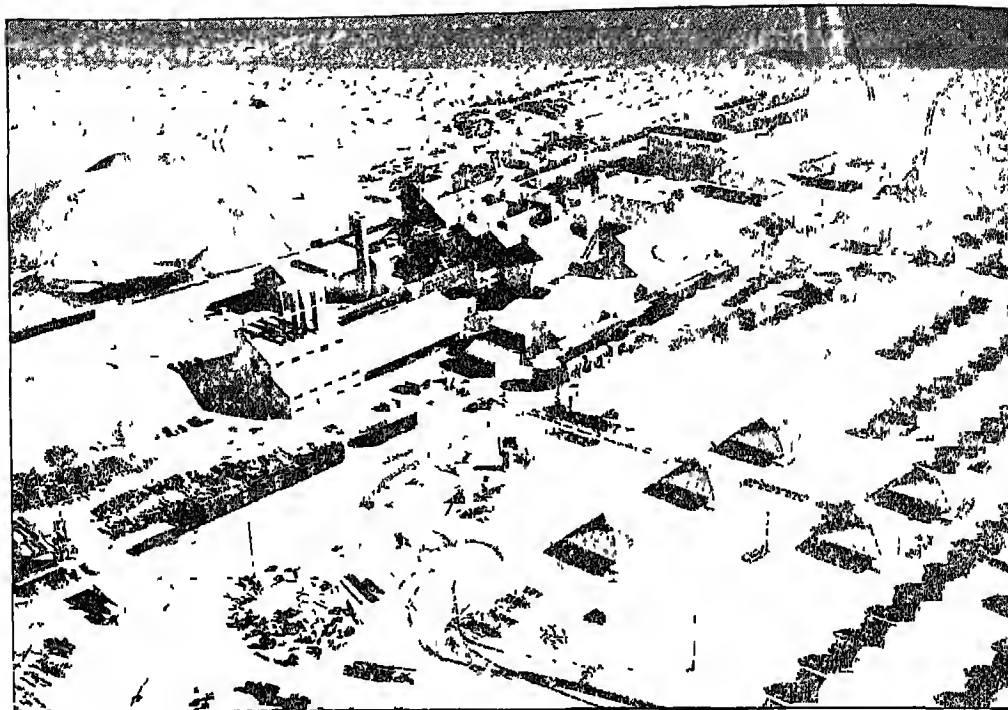


Some magnesium boride is formed at the



Courtesy of Libbey-Owens-Ford Glass Company

Figure 246 An installation of Hard Tempered Safety Glass in Stands of a Baseball Park. Balls and bats hurled against the glass had no effect. Spectators are given a clear view behind home plate.



Courtesy of Pacific Coast Borax Company

Figure 247 Plant Producing Borax at Boron, California

same time. The excess of magnesium and the oxides are dissolved in an acid, and the boron is recovered as an impure, brown, amorphous solid, which melts at about 2000° and solidifies to form a very hard and brittle product. Pure boron can be produced by reducing boron trichloride, BCl_3 , by means of hydrogen under the influence of an alternating-current arc.

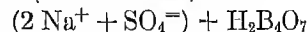
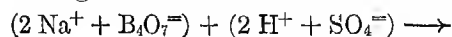
21 Properties

The element burns with a green flame and oxidizes slowly at lower temperatures. It combines directly with the halogens at elevated temperatures, except in the case of fluorine, in which it ignites spontaneously. Its halide compounds are BF_3 , BCl_3 , BBr_3 , and BI_3 . These compounds are not salts but resemble the halides of the non-metals — that is, CCl_4 , PCl_3 , etc. It forms a sulfide (B_2S_3) when heated with sulfur, and a nitride (BN) with nitrogen. It does not dissolve in acid but does dissolve in melted alkalis,

such as KOH , to form borates (K_3BO_3). It is oxidized by nitric acid to form boric acid (H_3BO_3). When heated with certain metals it forms borides (Mg_3B_2). In general, therefore, boron displays the chemical properties of a non-metal of valence number 3.

22. Boric Acid

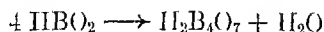
Orthoboric acid is usually prepared by heating a solution of borax with sulfuric acid



Since it is not readily soluble, boric acid precipitates as thin flakes, which are pearl-like in color, and which are unctuous to the touch. It is commonly known as *boracic acid*, and is used as an antiseptic, as a preservative, and as a glaze for some kinds of pottery. It is a weak acid. When heated moderately, boric acid loses a molecule of water and forms *metaboric acid*



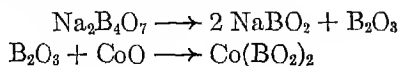
The *tetraboric acid* is formed upon further heating



23. Borax

Neutralization of boric acid by sodium hydroxide yields sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$. The hydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, which crystallizes from solutions at temperatures below 60° , is called *borax*. This substance is found, with calcium borate, in the Mohave Desert of California (page 539) and with potassium salts in Searles Lake (page 390). The minerals are converted into borax by treating them with water and adding sodium carbonate, which precipitates the calcium as calcium carbonate, and the borax is then crystallized by evaporating the solution. Rasonite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4 \text{H}_2\text{O}$), which is also mined in California, is a source of borax. When treated with water the insoluble portions of the deposit are removed by filtration, and the product obtained by evaporation is the decahydrate, borax.

Borax is used in making certain kinds of glass, enamels, and glazes. Its solution is alkaline, since boric acid is very weak, and for this reason it is used as a mild alkali to soften water; in soaps, as an antiseptic, and as a preservative. It is also used as a flux in certain metallurgical practices. When heated it melts and the liquid cools to give a glass. This glass dissolves the oxides of certain metals. For this reason borax is sometimes used to free metallic surfaces from coats of oxides before welding or soldering. Small beads of the glass are made to dissolve metallic oxides in testing for the presence of certain metals. Cobalt oxide, for example, dissolves to form a blue bead. These reactions depend upon the presence of an excess of the acid anhydride, B_2O_3 , in borax. The oxide of a metal reacts with this oxide to form a borate of the metal. The reaction may be explained by writing it in the form of the following equations



Borax is used in some kinds of glass to lower the melting point, to lower the coefficient of expansion, to increase the coefficient of refraction, and to decrease crystallization, to produce a high gloss on paper, as a mordant, and to clean hides and silk.

24. Other Compounds

Hydrides of boron — B_2H_6 , B_4H_{10} , B_5H_9 , $\text{B}_{10}\text{H}_{11}$ — are produced by the same methods as those of silicon. They are inflammable and react with water to form boric acid and hydrogen. *Sodium perborate*, $\text{NaBO}_3 \cdot 4 \text{H}_2\text{O}$, sometimes assigned the formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$, is a vigorous oxidizing agent. It is used in bleaching and as an antiseptic, especially in treating certain conditions of the mouth and gums. It is made by the action of hydrogen peroxide upon sodium borate. The *carbide* of boron, B_4C , is very hard, almost as hard as diamond. *Boron nitride*, BN , is produced when the element is heated to about 700° in the air, in pure nitrogen, or in nitric oxide. It is a white powder and is interesting because it is one compound that can be made from free nitrogen, without much difficulty, by the direct combination of the elements.

TITANIUM

25. Occurrence and Preparation

Titanium occurs in the soil and in many natural silicates in which it replaces a part of the silicon, which it resembles very closely. It is fairly abundant in the earth's crust but it is distributed widely and occurs in no concentrated deposits. It occurs as *rutile* (TiO_2) and as *ilmenite*, an iron ore (FeTiO_3). These minerals are obtained in this country from Virginia, California, and Florida. Titanium is produced by reducing the oxide (TiO_2) by means of carbon in an electric furnace. The product is not pure but contains carbon and nitrogen as the carbide and nitride of titanium. A more nearly pure form of titanium is made by reducing the chloride (TiCl_4) with sodium. An alloy, known as ferrotitanium and analogous to

ferrosilicon, is produced when titanium-bearing iron ores are reduced with carbon. This alloy is used in making titanium steel, the titanium serves, as silicon does, to remove impurities and gives a steel of great strength and possessing the ability to withstand sudden stresses or shocks.

26 Properties and Compounds

Titanium is silvery-white in appearance, its specific gravity is 4.5, and its melting point is about 1800°. Unlike silicon, it shows the properties of a metal in some of its compounds and those of a non-metal in others. The dioxide (TiO_2) resembles silica very closely, however, in acting as an acid anhydride. As such it forms titanate acids which resemble the various acids of silicon. These include condensed acids as well as acids analogous to ortho and metasilicic acid. Ilmenite, FeTiO_3 , for example, is a ferrous salt of metatitanic acid, H_2TiO_3 . The fluoride of titanium also forms fluorotitanic acid (H_2TiF_6), which is analogous to fluosilicic acid.

Besides the dioxide, the monoxide (TiO) and the trioxide (Ti_2O_3) are known. These are basic in character. Hence, titanium forms salts in which the element acts as a trivalent or a divalent metal. Examples of these compounds are the chloride, TiCl_3 , TiCl_2 , and the sulfate, $\text{Ti}_2(\text{SO}_4)_3$. Since titanium acts normally as a non-metal and forms stable compounds, such as TiO_2 , in which its valence number is positive 4, these salts are vigorous reducing agents. At high temperatures, titanium reacts with nitrogen to form the nitride, TiN . The tetrachloride, TiCl_4 , is not a salt. This substance hydrolyzes in moist air, producing dense clouds, and for this reason is used in making smoke-screens.

The dioxide, TiO_2 , which is white, is used as a pigment in paints, porcelain, and other ceramic products. Marketed under various trade names, titanium pigments can be secured in the form of lead titanate, the pure dioxide, or the dioxide mixed with barium, calcium, and magnesium pigments.

ZIRCONIUM AND HAFNIUM

Zirconium occurs in nature in the mineral called zircon, which is zirconium silicate, ZrSiO_4 , in baddeleyite, which contains the oxide, ZrO_2 , together with the oxides of silicon and other elements, and as the free oxide, zirconia. The most important deposits of these minerals are found in Ceylon, Brazil, Norway, and in North Carolina and Florida of the United States. The element forms an alloy with iron called *ferrozirconium* which is analogous to ferrosilicon. The free element can be produced in the same manner as free silicon and titanium. It has some use in radio tubes and in some flashlight mixtures.

Zirconium is much more metallic in character than silicon and titanium. It forms the dioxide and also probably the oxides, ZrO and Zr_2O_3 . The hydroxide corresponding to ZrO_2 dissolves in both acids and bases, and is consequently amphoteric. It dissolves readily in acids to form salts, such as ZrCl_4 , or *zirconyl* salts, such as ZrOCl_2 , in the latter, we may regard the hydroxide as reacting as the base $\text{Zr}(\text{OH})_4 - \text{H}_2\text{O} \rightarrow \text{ZrO}(\text{OH})_2$. When the hydroxide dissolves in bases, *zirconates*, such as Na_2ZrO_3 , are formed. The trichloride, ZrCl_3 , and the dichloride, ZrCl_2 , are both known.

The most important compound of zirconium is the oxide, ZrO_2 , which is used in making brick for lining furnaces, crucibles, and other utensils or articles which must withstand high temperature without melting. The oxide is well suited for these purposes since it melts at about 2700°, is resistant to chemical action, and has a small coefficient of expansion. In these respects it resembles quartz. It is used sometimes in making opaque glass and enamels.

Hafnium is one of the more recently discovered elements (1923). It resembles zirconium very closely, so closely in fact that, prior to the discovery of the element, it was present but unrecognized in all of the zirconium minerals and in the prepared compounds of zirconium. The compounds of

the element are, therefore, similar to those of zirconium. The only difference, as we might expect, is a slightly greater tendency of the element, its oxides, and hydroxides, to display basic properties.

Review Exercises

- Compare and contrast carbon and silicon, and the following compounds of the elements: the chlorides, the dioxides, the acids.
- What is silica gel? For what purposes is it used?
- What are the formulas of the sodium salts of orthosilicic acid, metasilicic acid, orthoboric acid, metaboric acid, one disilicic acid, and one trisilicic acid?
- What is a *condensed acid*? Show the relation of the condensed silicic acids to H_2SiO_4 .
- Identify: water glass, quartz, borax, $CaSiO_3$, rock crystal, ferrosilicon, fluosilicic acid, diatomaceous earth, orthoclase, zirconia, H_2TiO_3 , rock or mineral wool, hafnium.
- Why are solutions of sodium silicate and borax alkaline?
- Explain the use of borax in soap, in cleaning metallic surfaces, and in analytical chemistry where it is used in testing for certain metals.
- What is the chemical nature of glass? What is the difference in composition between soft and hard glass? How does the composition of Pyrex glass differ from that of ordinary soft glass?
- Why is calcium carbonate added to the charge of blast furnaces in which iron ores are reduced to metallic iron?
- In what respects are boron and its compounds similar to silicon and its compounds and in what respects are they different?
- How is borax prepared from colemanite and from tincalconite?
- How does the abundance of silicon and its compounds in nature compare with the abundance of carbon and its compounds? Can you point out similar cases in which there is a great difference in the relative abundance of the first and second elements in a periodic group?
- What is a flux? With what kinds of substances do boron trioxide and silicon dioxide act as fluxes?
- Write an equation to show how boric acid, H_3BO_3 , can be prepared from borax.
- What is the general method of preparing the free elements, boron, silicon, titanium, zirconium, phosphorus, arsenic, antimony, and bismuth from their oxides?
- How would you proceed to prepare the following substances in succession, starting with silica? Na_2SiO_3 , H_2SiO_4 , SiF_4 , and $CaSiO_3$.
- How would you proceed in preparing fluosilicic acid from silica?
- For what purposes is ferrosilicon added to iron in making steel? What is the composition and general properties of Durodon?
- Using the percentages given in Table 31, calculate the weights of SiO_2 , Na_2CO_3 , and $CaCO_3$ required to make one ton of soda glass.
- What weight of aluminum is required to produce a ton of silicon by the reduction of silica?
- What is the percentage of silicon in beryl?
- A certain silicate mineral was found to contain 17.48 per cent of magnesium, 9.6 per cent of calcium, and 26.89 per cent of silicon. The remainder was found to be oxygen. What is the simplest formula of the silicate, and what is it?
- Outline a method involving a series of reactions that can be used to produce silica gel from sand.
- An iron ore contains three per cent of silica. What weight of calcium carbonate (limestone) is required as a flux for each ton of ore?

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COLLOIDAL DISPERSIONS

1. Introduction Explanation of Terms

In our study of solutions we learned that they are apparently homogeneous mixtures of two or more substances, and that the particles of both solute and solvent are of approximately molecular, or in some solutions of ionic, dimensions. We may think of the molecules or ions of the solute as dispersed, or scattered, in the solvent. We are now to consider dispersions of particles of somewhat larger magnitudes, yet not large enough to be seen with a microscope.

If an insoluble solid is finely powdered and is then thoroughly mixed with water, it may remain suspended for some time. But the particles of the solid are usually visible, they can be separated from the liquid by filtration, and if more dense than water, they will settle to the bottom of the container after some time. Between this kind of suspension and a solution there are other mixtures that contain one substance dispersed in an extremely fine state of division in another substance. The particles of these mixtures are not visible, they cannot be separated by filtration, and they do not settle out of the mixture. This kind of suspension is called a *colloidal dispersion*, and the dispersed substance is said to be in the *colloidal state*. The substance in which the particles are suspended is called the *dispersing medium*, and the two substances together make a *colloidal system*. A colloidal dispersion in a liquid is called a *sol* and, when the medium is water, the dispersion is a *hydrosol*. When a sol is coagulated it is then called a *gel*.

It is evident that there is no definite dividing line between the colloidal state and true

solutions, on the one hand, and the colloidal state and ordinary mixtures of particles of solids and liquids (or any other states of matter) on the other. The differences among the three kinds of mixtures depend largely upon differences in the sizes of the particles of the substances which make up the mixture. When the particles of the dispersed substance are smaller than one millionth of a millimeter (one *millimicron*, $m\mu$) in diameter, the mixture begins to exhibit the properties of a true solution. These properties include the effects of the solute upon the vapor tension, boiling point, and freezing point of the solvent. Colloidally dispersed particles are, in general, those whose diameters lie within the range of $1\ m\mu$ to $100\ m\mu$. Above $100\ m\mu$, the particles become visible with the aid of a powerful microscope, and the mixtures behave as ordinary suspensions. We must understand, however, that the smallest particle of a dispersed substance that shows colloidal characteristics may consist of several thousand molecules.

2. The Colloidal State of Matter

The form and physical characteristics of colloidally dispersed particles vary widely. They may be grains, droplets, bubbles, or even films and filaments, if the films are thin enough and the filaments are small enough in diameter to come within the range of colloidal dimensions. Colloidal suspensions *appear* to be homogeneous, but they differ widely from true solutions. Such mixtures have negligible osmotic pressures, and their freezing and boiling points are approximately

the same as those of the pure liquid in which the suspensions exist

The name colloid was suggested by Graham (1861). The word comes from the Greek word *kolla*, which means *glue*. Graham used this term to distinguish certain substances from *crystalloids*, which form true solutions. We now know that the colloidal state of some substances is more easily produced than that of others, but this state is not peculiar to any one group of substances. Any substance may so exist under suitable conditions. Sodium chloride is a substance that we should least expect to find in any but a crystalline state or in a true solution. But if sodium and chloride ions form sodium chloride in a liquid in which salt does not dissolve, the product may be obtained as a colloidal dispersion. Even ice may exist as a colloid when the water dissolved in certain organic liquids is cooled below its freezing point. In general, there is but one limitation: the colloidal state of one substance cannot be produced in another in which it is soluble.

3 Kinds of Colloidal Dispersions and Their Importance

Suspensions in which a liquid acts as the dispersing medium are most familiar and most important, but in other cases the dispersing medium may be a gas or a solid, and the dispersed substance may be a liquid, a gas, or a solid. With the exception of a gas dispersed in a gas, the parts of a colloidal system may represent any states of matter. Fog (liquid in a gas), foam (gas in a liquid), and smoke (solid in a gas) are, or may be, colloidal dispersions. The blue color of some crystals of rock salt is due to the colloidal dispersion of metallic sodium in the salt (solid in a solid). White flowers and gray hair contain dispersed air bubbles (gas in a solid).

Since it applies to so many different systems and, under certain conditions, to almost every substance, information concerning the colloidal state is of great value in industry,

in agriculture, in medicine, and in fact wherever materials are used. Glue, clay, rubber, bakelite, glass, paints, varnish, cements, lubricants, and soap contain materials in the colloidal state. The living cell is largely colloidal in character. Its wall is colloidal, and within it there is a jelly-like dispersion. The protoplasm of every cell in the animal body is a colloid. So, too, are the various structures of plants. In short, we may say that living tissue is colloidal, and the various activities in which it is involved in life processes are largely those concerned with the chemistry of the colloidal state.

The chemistry of the colloidal state of matter is of great importance in physiology and medicine, because it concerns practically every problem of life processes — nutrition, digestion, secretion — and the more general problems of the body's structure and state of health. Colloidal chemistry is also important in the manufacture of paper, textiles, the tanning of leather, the manufacture of rubber goods, in the production of photographic plates and films, varnishes, glue, inks, plastics, cements, pottery, dairy products (butter, cheese, etc.), salad dressings, food products of all kinds, and in many other industries. The soil contains many colloiddally dispersed substances, and the physical condition of the soil, which is often of great importance — as important as the compounds present — is, principally, a matter involving these colloidal systems.

4. The Colors of Colloidal Dispersions

The deep blue color of some lakes is produced by colloiddally dispersed material in the water, and the blue of the sky is caused by colloidal dust. Colloidal dispersions are responsible for blue glass, blue eyes, and blue feathers. The small particles of colloidal dispersions absorb certain colors, or wavelengths, from white light, depending upon their dimensions. The colloidal dispersions of the same substance may therefore show several different colors under different condi-

tions. Thus, colloidal gold suspensions in water may be red, green, blue, or violet.

5 Classes of Colloidal Dispersions in a Liquid

If we confine our attention for the present to dispersions in a liquid — these are most important — they may be divided into two classes: *lyophilic* and *lyophobic* colloids, or if the liquid is water, *hydrophilic* and *hydrophobic* colloids. The former are substances that naturally form colloidal suspensions when mixed with the liquid without the employment of any special methods of preparation. They include glue, starch, gums, and proteins, such as gelatin and albumen. Lyophobic colloids are, for the most part, elements or compounds of an inorganic character. They must not be soluble in the dispersing medium. Special methods (see next section) must be employed to prepare stable suspensions of these substances. Lyophilic colloids appear to possess an attraction for the liquid, thus becoming highly *solvated* — combined with the solvent, as in a hydrate. Many substances that act in this manner, the proteins for example, consist of very complex molecules, and their molecular weights may reach 100,000 or more. In some of these mixtures the colloidal particles may be these very large molecules.

Lyophilic colloids are *reversible*, which means that when they are precipitated from the dispersed state, they can be converted once more to that condition when the liquid is added to them. Thus, albumen can be precipitated by the addition of a concentrated solution of a salt, but it will be redispersed if thoroughly washed and placed in pure water. Even when dried, it slowly redisperses when water is added. Lyophobic colloids are not reversible; when they are once precipitated, they are not redispersed when the liquid is again added. This group of colloids is not solvated, or at most only slightly solvated, by the dispersing medium.

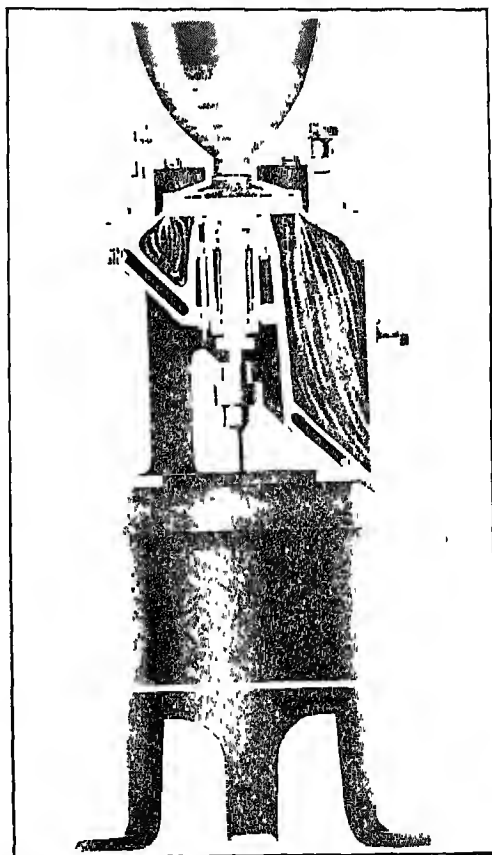
The names *suspensoids* and *emulsoids* are sometimes used instead of lyophobic and lyophilic colloids. The former terms are more

general in meaning. *Suspensoids* may refer, for example, to fog, foams, or suspensions of gases or solids in solids, while the term *lyophobic colloid* is applied only to a suspension of a solid in a liquid.

6 The Preparation of Colloidal (Lyophobic) Dispersions

Solids can be dispersed to form lyophobic suspensions by several methods which are classified as (1) dispersion or (2) condensation methods. We shall speak only of suspensions in water.

(1) *Dispersion Methods* These methods of producing colloidal suspensions involve the subdivision of coarse particles of the substance into particles of colloidal dimensions. Grinding or other purely physical operations



Courtesy of Premier Mill Corporation

Figure 248 A Colloid Mill

are used for this purpose. The *colloidal mill* is a machine especially designed to produce the required state of division, it is used in many industries. The dispersion is sometimes effected by adding to the medium a second substance that acts upon the grains of the first substance to break them up into particles of colloidal size. The substance that acts in this manner is called the *peptizing agent* and the process is called *peptization*. Thus, a dilute solution of sodium hydroxide peptizes clay.

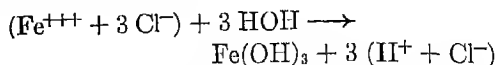
The liquid medium, itself, sometimes causes the peptization of certain solids. Thus, glue and gelatin are peptized in water without the aid of a mechanical device or a chemical peptizing agent. Shellac, resins, and certain gums form similar colloidal suspensions in other liquids. All these are examples, of course, of lyophilic colloids, or emulsoids.

Colloidal dispersions of metals below hydrogen in the electrochemical series can be produced in water by the *Bredig arc process*. Metals above hydrogen are dispersed by the same process in liquids other than water. Two wires of the metal are allowed to dip under water. The outside ends of the wires are attached to an electrical circuit. The ends under water are separated slightly, and an electric arc is produced between them. Small particles of the metal are split off of the wire and become dispersed in the liquid. Similar particles may be produced by the condensation of the vapor of the metal which is volatilized at the temperature of the arc.

(2) *Condensation Methods* These methods involve the formation of particles of colloidal dimensions by causing smaller particles, molecules for example, to aggregate. They depend upon chemical reactions, between the molecules or ions of two substances, in which insoluble products are formed. The particles of the product must remain within the range of colloidal dimensions; otherwise, of course, they would form the larger aggregates that make up what we usually call a precipitate.

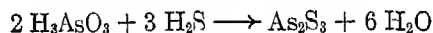
The reactions employed to produce col-

loidal dispersions by condensation methods are usually (1) *double decomposition* or (2) *reduction*. A dark red suspension of ferric hydroxide¹ is formed by mixing a concentrated solution of ferric chloride with hot water. This reaction is a double decomposition (hydrolysis)



The formation of colloidal suspensions of the hydroxides of the metals explains why precipitates do not always form when the salts of the metals hydrolyze, although the hydroxides of most of the metals are only slightly soluble. When the salts are dissolved in water there is no precipitate, although we are certain that they have reacted in some cases to an appreciable extent to form the hydroxide and to liberate the acid. The insoluble hydroxide remains in the liquid in the colloidal state.

A colloidal suspension of arsenious sulfide is produced by the reaction of hydrogen sulfide and arsenious acid in the absence of electrolytes such as hydrochloric acid



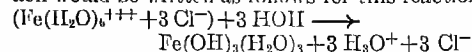
As examples involving reduction, we may take the formation of a colloidal gold dispersion by the reduction of gold (aure) chloride in dilute solutions by such substances as tannin, hydroquinone, formaldehyde, and ferrous sulfate.

PROPERTIES OF COLLOIDAL SYSTEMS

7. The Tyndall Effect

When a beam of light enters a darkened room through a small opening in a window

¹ Merely as a matter of convenience, we have indicated the substance produced in this reaction as the hydroxide, $\text{Fe}(\text{OH})_3$. It is probably more nearly accurate to consider the reaction as one that involves the hydrolysis of the hydrated ferric ion $\text{Fe}(\text{H}_2\text{O})_6^{+++}$, to form $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$. The equation would be written as follows for this reaction



The hydrated ferric ion acts as an acid and water as a base.

shade, small particles of dust, which are not visible in a well-lighted room, can be seen. Many of these dust particles are of colloidal size. They are observed in the darkened room as tiny bright flashes, because they reflect light in all directions, as they move in a more or less random manner in its path. Although the observer may be at right angles to the path of the beam, some of the light reaches his eye. The same phenomenon can be observed by passing a beam of light through a colloidal dispersion (Figure 88). The dispersed particles act in the same manner as the dust particles and scatter the light in all directions, thus making the beam's path through the mixture visible. The illumination in this manner of the beam's path through a liquid is called the *Tyndall effect*. Each solid particle in the dispersion becomes a source of reflected light, although the particles are too small to be seen with the help of the most powerful microscope. The ultramicroscope is based upon the Tyndall effect. An intense beam of light is passed through the colloidal dispersion which is contained in a small cell. A microscope is focused upon the contents of this cell, which is observed against a dark background. We do not actually see the particles suspended in the liquid. We are, however, made aware of their presence by their effect in scattering and reflecting the light that falls upon them.

True solutions do not show the Tyndall effect. This, then, is a method by which a true solution and a colloidal suspension can be distinguished.

8 The Brownian Movement

When colloidal dispersions in a liquid medium are examined by means of the ultramicroscope, the particles are seen to be in constant motion (Figure 249). A particle moves in a straight line for a short distance in one direction, and then suddenly changes the direction of its path. This phenomenon was first observed and reported by a botanist, Brown, in his studies of pollen dust suspended in water. It is now called the Brown-

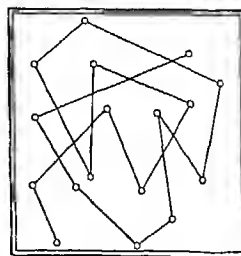


Figure 249 The Brownian Movement

ian movement. It provides one of the most convincing arguments in favor of the molecular states of liquids and gases. If the liquid in which the small particles of solid are dispersed consists of molecules, and if these are moving, they will collide with a colloidal particle. The latter, being free to move, will travel in a straight line until the direction of its path is changed by collision with other molecules of the medium. The impacts against all sides of a very small particle usually do not balance, as they would for a larger particle in the body of a liquid (Figure 250). Consequently, the particle is urged first one way and then another. The Brownian movement of colloidal particles is one reason why they do not settle.

9 Electrical Charge

In general, the particles of lyophobic dis-

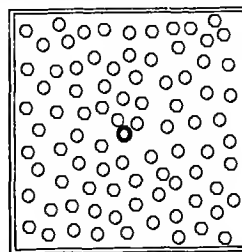
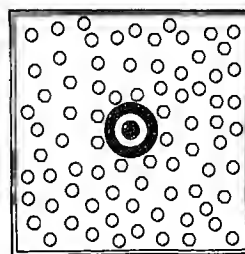


Figure 250 Impacts of Molecules of Solvent with Large Particle (top) and with Small Particle

pensions are electrically charged. The presence of electrical charges can be demonstrated by placing electrodes in a colloidal suspension of arsenious sulfide. The dispersion is found to be a conductor. The colloidal material, which has a yellow color, moves toward the anode and is therefore negatively charged. At the anode, the electrically charged particles are discharged, and the colloidal dispersion is converted into a precipitate. It seems, therefore, that the electrical charges of the particles are necessary, in some way, to the colloidal state of this substance. All the particles possess the same kind of charge. Most of the sulfides of metals and the metals themselves form negatively charged colloidal dispersions. The hydroxides of the metals, such as ferric hydroxide, have positive charges.

The charges of colloidal particles probably result from the adsorption of ions which exist in the medium. These ions are frequently hydrogen or hydroxyl ions. If the particles adsorb positive ions more readily than negative ions, they acquire a positive charge and *vice versa*. It is really the charge of the adsorbed ions that causes the colloidal particles to move under the influence of a difference in electric potential. Since all the particles of one kind carry the same kind of charge, they repel one another. This condition prevents them from coalescing to form larger aggregates, and is one more reason why they remain suspended instead of settling. The adsorbed ions act as the peptizing agent.

10 The Effect of Electrolytes upon Colloidal Dispersions

Many cases are known in which ions are responsible both for peptization of a colloid and also for coagulation or precipitation. If silver bromide is formed in the presence of an excess of silver ion, the particles of silver bromide adsorb silver ions and become colloiddally dispersed, thus failing to precipitate. These particles, of course, are positively charged. If the bromide ion is present in excess, it is adsorbed, and a negatively

charged dispersion of silver bromide results. On the other hand, a dispersion of arsenious sulfide is readily coagulated by the addition of hydrochloric acid. The negative charge of the particles is due to the adsorption of hydroxyl ions. The addition of the acid removes these ions from their adsorbed state and converts them into water molecules. Hence the arsenious sulfide particles lose their negative charges, and can then form larger aggregates. Not only does hydrochloric acid precipitate arsenious sulfide from its dispersed state, but salts, such as sodium or ammonium chloride, do the same. The addition of an excess of positive ions of any kind neutralizes the negative charge carried by the particle. This effect results from the tendency of the ions adsorbed by a colloidal particle to attract ions of the opposite sign, thereby decreasing, or even completely neutralizing, the charge on the particle.

As a general rule, we may say that colloidal dispersions are likely to be produced in solutions containing low ionic concentrations. When once formed, they are likely to be coagulated by the addition of high concentrations of ions whose charges are opposite in sign to those which are adsorbed.

The effect of ions upon colloidal dispersions is shown when river waters, which contain considerable material in colloidal suspension, flow into the sea. The salts of sea water cause these colloids to be precipitated, and the deposit of this material leads eventually to the formation of a delta.

In the laboratory, precipitates frequently must be washed to remove other substances that may be present in the solutions that wet them. If a precipitate is to be dried and weighed as arsenic trisulfide, for example, other substances, such as sodium chloride, must be removed by washing to prevent an error in the estimation of the weight of the arsenic trisulfide. During the washing, the precipitate may be changed into the colloidal state, and if this happens, it will be lost by passing through the filter. This condition may result when the water used in washing removes certain ions that counteract the effect of the ions that

were originally adsorbed by the colloidal particles, and that are responsible for the electrical charges of these particles. To prevent the formation of the colloidal state during washing, ammonium salts, which can be removed later by heating the precipitate — because the ammonium salts decompose when heated — are added to the water used for washing. The ions of the ammonium salt replace the ions removed by the water and thus prevent the formation of a dispersion.

11 The Electrical Charge of Lyophilic Colloids

The same lyophilic colloid may exist in a dispersion with no electrical charge, or it may be either positively or negatively charged. The kind of charge depends upon the hydrogen ion concentration of the medium. Many of these substances are amphoteric. In a strongly acid medium they attract hydrogen ions and become positively charged. In an alkaline medium they give up hydrogen ion (from some part of their own structure), and therefore possess a negative charge. At a certain pH of the medium the colloidal particles have no charge. This condition of the medium is called the *isoelectric point* of the colloidal dispersion.

12. The Precipitation of Colloidal Dust Particles

The *Cottrell electrical precipitator* is used to recover substances from smokes or fumes and to prevent smoke from furnaces. The escaping gases are passed through a space across which there is a high voltage, or difference of potential. The small particles of the smoke — chiefly solid particles — are colloiddally dispersed in air or in other gases. In the electric field these particles become charged by induction and act, therefore, in the same manner as colloidal dispersions in a liquid. In the Cottrell process the particles are attracted to the highly charged electrodes, where they are discharged and deposited as dust. The process is used to recover valuable products that otherwise would escape from the stacks of smelters, kilns, and furnaces. Potassium salts may thus be recovered from the dust of cement kilns, selenium from the dust of pyrites

burners, and valuable metals or their compounds, which would otherwise be lost, may be precipitated in the flue dust from smelters and foundries. The Cottrell process is also used to prevent or lessen the "smoke nuisance" in industrial centers. Ordinary smoke is black because it contains unburned particles of carbon and other substances, both solids and liquids. These may be precipitated in the same manner as other small particles that are colloiddally dispersed.

13. Dialysis

Since high concentrations of ions tend to precipitate colloids, these ions must be removed if the colloidal dispersions are to remain in a stabilized condition for any length of time. This removal may be effected by taking advantage of the fact that colloids will not pass through many kinds of membranes permeable to water and to the ions of electrolytes dissolved in the water. Ordinary filter paper is permeable to colloids as well as to water, ions, and the solutions of other substances, but certain kinds of membranes, such as egg skin, parchment paper, cellophane (not the waterproof variety), and bladder, will hold back the colloidal dispersion, thus permitting it to be separated from substances that are in true solution. This process is called *dialysis*.

To show dialysis, make a bag from a sheet of parchment paper and place in it a freshly prepared colloidal dispersion of ferric hydroxide. This dispersion contains hydrochloric acid which is to be removed by dialysis. The bag is then suspended in a vessel filled with water. If this water is changed frequently, the acid passes through the membrane, and a very pure and stable suspension of ferric hydroxide may be obtained. The passage of the acid through the walls of the bag may be verified by testing the solution in the beaker for chloride ion by means of silver nitrate.

A filter which will retain colloidal particles is called an *ultra-filter*. The filtering material in such a device is really a colloid itself. A layer of jelly (gelatin, silicic acid, or the like) is supported on porous porcelain or filter paper, and the

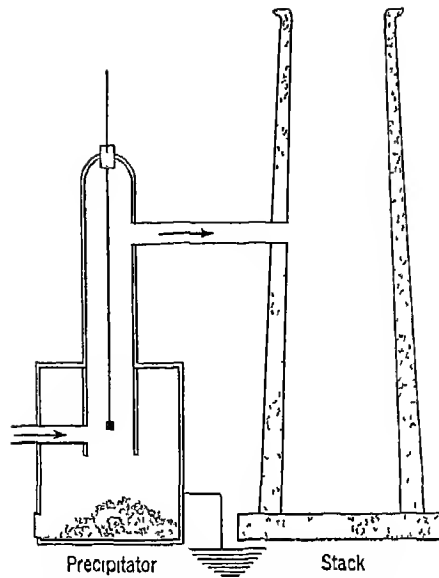
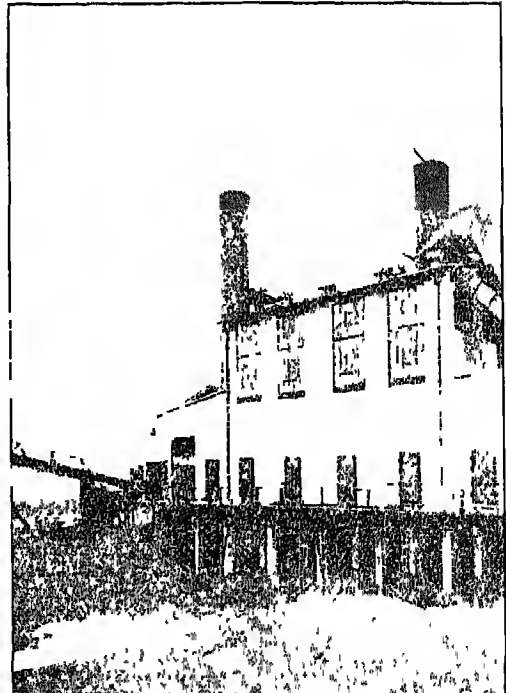
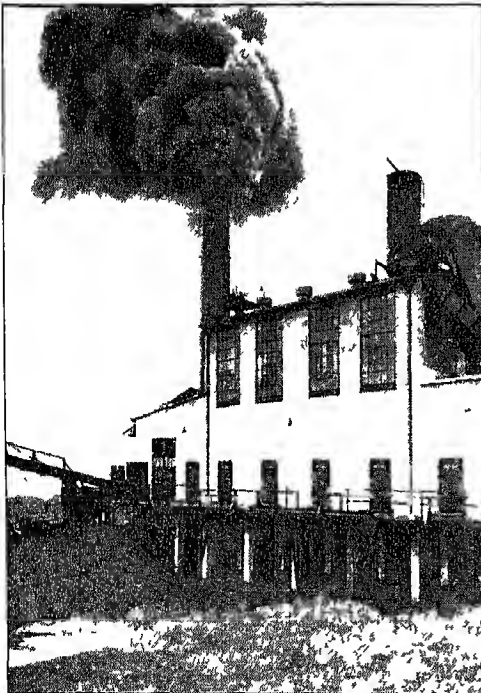


Figure 251 Cottrell Electrical Precipitator



Courtesy of Western Precipitation Corporation

Figure 252 Electrical Precipitator

The effect of the precipitator on smoke from a lamp black briquetting plant is shown in the right-hand picture. The picture on the left was taken before the precipitator was installed.

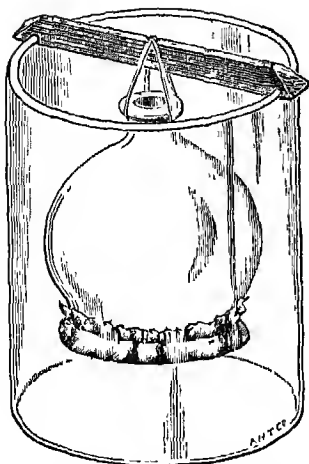


Figure 253 Diagram of Cell Used for Dialysis

The ferric hydroxide dispersion is retained in the bag, while the hydrochloric acid diffuses through the parchment and into the pure water

liquid medium in which the colloid particles are dispersed is forced through it when pressure is applied. The colloidal material remains behind on the layer of jelly. The ultra-filter is of considerable use in removing colloids from solutions of soluble substances, in identifying various materials as colloidal dispersions, and in concentrating and studying various colloidal substances, such as enzymes and bacterial toxins, that occur in very small amounts in a liquid medium.

14 Protective Colloidal Substances

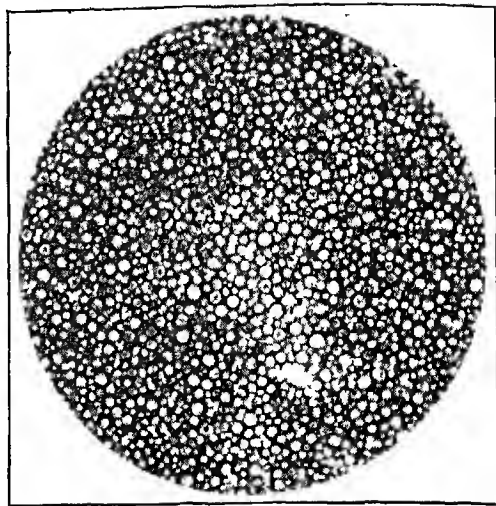
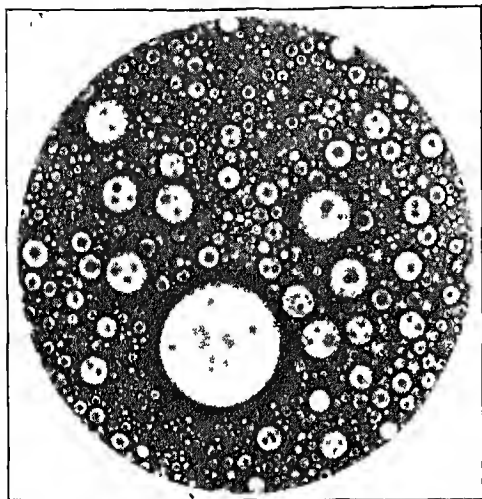
In some colloidal systems the coagulation of one colloid may be prevented by the presence of another. The second colloid probably forms a *protective* film or coat around the particles of the first, thus preventing them from coming into direct contact and coagulating to form large particles that would not remain in suspension. Gelatin is the most familiar and widely used protective colloid. Its action may be demonstrated by mixing a solution of potassium bromide with a solution of silver nitrate that contains about one per cent of gelatin. Naturally, we should expect a precipitate of silver bromide to form, but there is none. We may assume that the gelatin prevents the formation of a precipitate by forming a protective film around grains of the silver

bromide of colloidal size. The gelatin that coats photographic plates and films maintains the colloidal dispersion of the silver salts, which are prepared in this manner. Many suspensions are more stable if they are formed in the presence of gelatin. This is true, particularly, of suspensions of the metals. Gelatin acts as a protective colloid in the manufacture of ice cream, in which it prevents the formation of crystals of ice and sugar. Gum arabic acts in similar capacity in marshmallows and in inks. Lactalbumen in milk acts as a protective colloid in producing curds of smaller particles, when the casein of the milk is coagulated in the stomach. Glue, starch, and similar substances are used as protective colloids in mixtures that are added to the water in boilers to prevent the formation of scale.

15 Emulsions

An emulsion is a dispersion of very small drops of one liquid in another, with which it is not miscible. We may prepare an emulsion of kerosene and water by violently shaking the two liquids together. A milky fluid, consisting of thousands of drops of one liquid in the other, is the result. This emulsion, however, is only temporary. Water has a high surface tension, and in attempting to reduce their surface, the small drops of this substance coalesce to form larger drops, until, finally, the water separates entirely from the oil to form a distinct layer.

To prepare a stable emulsion, we must employ a third substance called the *emulsifying agent*. This substance must prevent the separation of the liquids into two layers. The emulsifying agent may produce two effects: (1) It may decrease the surface tensions of the liquids, thereby lessening the tendency of small drops of each to coalesce to form larger ones, (2) It may form protecting layers or films about the drops of one of the liquids. Soap, for example, is an emulsifying agent for a mixture of kerosene and water. With ordinary soaps, drops of oil are dispersed in water. Calcium soaps



Courtesy of Premier Mill Corporation

Figure 254 An Ordinary Emulsion at left and Emulsion Processed Through a Colloidal Mill at right

cause drops of water to be dispersed in the oil. In this connection it should be said that ordinary soap is a colloid which is peptized by water. Calcium soap, which is not peptized by water, is readily peptized by oils. The general rule, therefore, is that the liquid which peptizes the colloidal emulsifying agent will act as the dispersing medium for the second liquid of the emulsion.

The cleansing action of soap depends chiefly upon its action as an emulsifying agent in forming stable emulsions of water, oils, and grease. Milk is an emulsion of drops or globules of butter-fat in water, with casein serving as the emulsifying agent. When the milk "sours," because of the formation of lactic acid, the emulsifying agent is precipitated and the emulsion is no longer stable. When this happens, fat is readily separated from the water as butter, which is, itself, really an emulsion of *water in butter-fat*. Mayonnaise is an emulsion of olive oil in dilute vinegar, for which the yolk of eggs, which is a colloidal material, acts as the emulsifying agent. Soap is the emulsifying agent in emulsions of water and certain coal-tar products known as cresols that are used in making disinfectants.

The stability of an emulsion depends upon

the emulsifying agent. Hence, an emulsion may be destroyed by the addition of a substance which converts the emulsifying agent into another substance. Thus, an emulsion of oil and water in which a sodium soap is the emulsifying agent may be broken up by adding an acid, which reacts with the soap to form a sodium salt of the acid added and the free acid (stearic, oleic, or palmitic) of which the soap was originally the sodium salt.

16. Jellies

When an emulsoid "sets," it forms a *jelly*, sometimes called a *gel*. The acidification of a solution of sodium silicate causes the formation of a *jelly* of silicic acid (page 534). It is thought that the silicic acid forms a cell-like mass, the walls of the "cells" are made up of filament-like structures, which are composed of strings of united particles. Inside these cells the liquid is held in about the same way as a sponge holds water. When the jelly is partially dehydrated, a porous product, called *silica gel*, results (page 535).

The filaments largely responsible for the structures of jellies are highly hydrated materials. This is true, for example, of the protein-containing tissues of the body, which readily hydrate and are present as

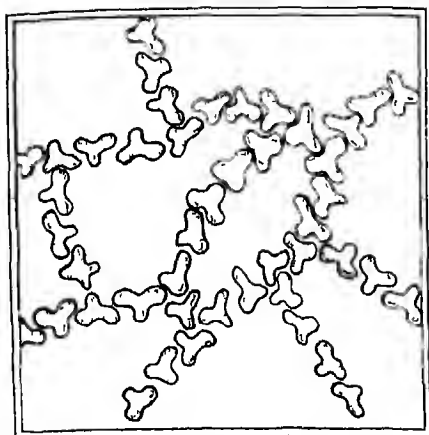


Fig 255 The Structure of a Gel

gels in the body. Undue hydration of these tissues produces swelling, or oedema. The swelling and bursting of seeds planted in the soil is a process that depends upon the hydration of colloidal material.

Fruit jellies are made from acid-containing juices of certain fruits, sugar, and pectin, which is a natural constituent of some fruits, such as apples and grapes. The acid aids in the hydration of the pectin and in the formation of the jelly. Soap is a jelly (partially dried), and agar is a dry form of silica jelly. Solid alcohol is a jelly prepared from soap and alcohol, calcium acetate and alcohol, or cellulose nitrate or acetate and alcohol. The alcohol is held in the cell-like pores of the other substance. Other familiar jellies are gelatin dynamite (page 485), "gelatin desserts," photographic films, and many preparations containing hydrated starch.

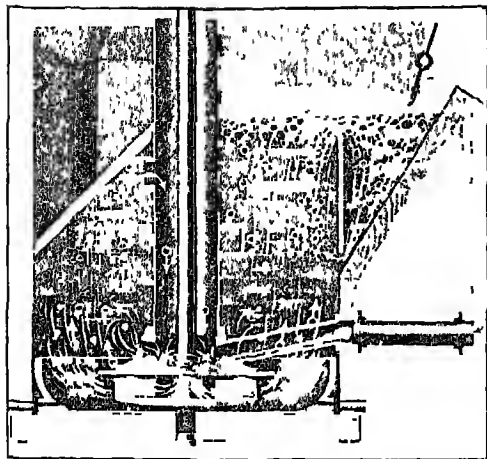
17 Adsorption

Adsorption refers to the tendency of particles (usually molecules or ions) of one substance to adhere to the surface of certain solids or liquids. This term should not be confused with absorption which refers, for example, to the taking up of water by a sponge, or to the penetration of a solid by a liquid or a gas because of the porosity of the

solid. Adsorption is largely a surface phenomenon, consequently, the power of adsorption that a solid or a liquid possesses depends upon the amount of surface that it exposes to the particles of another substance, as well as upon its chemical nature. A cube which is one centimeter in length along each edge has only six square centimeters of surface, but if this same cube is broken up into particles of colloidal size, the total surface is measured in thousands of square meters. Colloidal particles, therefore, show extremely great adsorptive powers. In fact we may define colloids as substances which have been so finely divided that surface effects play an important part in determining their properties. Then adsorption of ions is responsible, at least in part, for their electrical charge. Certain materials, even when they exist as particles larger than those that lie within the range of colloidal dimensions, also adsorb liquids and gases, and when placed in solutions they may also adsorb molecules or ions. For all of these materials adsorption depends upon the extent of surface, and therefore increases as the size of the particles decreases. Not all liquids, solids, gases, or ions are adsorbed equally readily or to the same extent by any one material. As already stated (page 291), the charcoal used in gas masks adsorbs some gases very readily and others not at all under ordinary conditions.

18 The Flotation Process of Concentrating the Ores of Metals

The ores containing valuable metals are mixed with earthy material, from which they must be separated before the metal is recovered. Some ores contain less than one per cent of the metal. Any effective method of concentrating them will make possible the recovery of the metal without the presence of extremely large quantities of inert and worthless material to interfere in the metallurgical reactions and operations involved in the extractions. One process employed for this purpose is called *flotation*.



Courtesy of Denver Equipment Company

Figure 256 Diagrammatic Sketch of a Flotation Cell

The ore is crushed and thoroughly mixed with water to which about one per cent of some oil — often pine oil — has been added. A froth is produced by vigorously churning air into the mixture or by blowing air into it. A small quantity of an organic compound (several different ones are used) is also added. This substance must be one that is adsorbed on the surface of the mineral particles that are to be recovered. The adsorbed substance also prevents these particles from being wetted by water. They are, therefore, more likely to become attached to bubbles of air in the froth, with which they rise to the top of the flotation cell. Other particles of the ore that do not adsorb the compound that is added are wetted easily by water and sink to the bottom of the cell. This material contains most of the valueless portion of the ore. Sometimes, however, the process is reversed. The froth flows over the rim of the vat (Figure 256), and from it there is recovered a highly concentrated form of the valuable portion of the ore. The flotation process is applicable, most generally, to ores containing free metals or sulfides of the metals, and finds its greatest use in the concentration of ores of lead, zinc, and copper. The process makes possible the use of low-grade ores that otherwise could not be worked except at prohibitive cost.

Review Exercises

- 1 Explain the meaning of the following terms and give an example of each: lyophobic colloid, lyophilic colloid, emulsion, hydrosol, protective colloid, dialysis.
- 2 Describe the Tyndall effect and tell how it may be used to detect colloidal dispersions. Which class of suspensions would you expect to show the more pronounced Tyndall effect?
- 3 Describe and explain the phenomenon known as the Brownian movement.
- 4 Define adsorption. What part does it play in the formation of colloidal suspensions?
- 5 Why is a colloidal suspension more stable after it has been dialyzed than before?
- 6 Define peptization. What are some of the methods by which colloids are peptized?
- 7 How are colloidal dispersions different from solutions?
- 8 Explain the action of soap as a cleansing agent in removing oil and dirt.
- 9 What is the nature of the dispersing medium and the dispersed substance in cheese, cake, whipped cream, and milk-glass?
- 10 How does dialysis differ from osmosis?
- 11 What procedure can you suggest as a method of producing a colloidal dispersion of (1) clay, (2) silver, (3) aluminum hydroxide, or hydrated aluminum oxide, and (4) the sulfide of antimony?
- 12 Why does arsenic trisulfide precipitate instead of forming a colloidal dispersion in the presence of hydrochloric acid?
- 13 How are soluble salts that are useful as fertilizers held in the soil instead of being carried away immediately by water?

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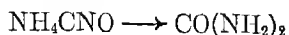
ORGANIC CHEMISTRY: THE HYDROCARBONS

Organic chemistry appears to me like a primeval forest of the tropics, full of the most remarkable things

WOHLER TO BERZELIUS

1 Introduction

During the eighteenth century, chemists were very much interested in substances associated with plants and animals. These substances were classified as *organic*, while substances of a mineral character were classified as *inorganic*. All organic compounds were recognized as containing carbon, consequently, organic chemistry came to be identified, also, as the branch of the science which deals with the compounds of that element. Until 1828, it was thought that organic compounds could be produced only in nature by organisms, and that it was impossible to produce them from inorganic substances. But in that year, Wohler converted ammonium cyanate (NH_4CNO) — a compound not related in any way to plants or animals and usually regarded as inorganic — into the compound urea, $\text{CO}(\text{NH}_2)_2$. Most of the nitrogen which is eliminated from the bodies of animals, as a result of the oxidation of nitrogenous waste materials, is found in the urine as urea. Wohler's synthesis, therefore, produced an organic compound from an inorganic compound, which is not associated in any way with living objects. Urea and ammonium cyanate contain the same numbers of carbon, nitrogen, and oxygen atoms per molecule, but the atoms are differently arranged.



Wohler's discovery marked the beginning of modern organic chemistry. Since 1828, many thousands of organic compounds have been synthesized. Some of them are substances that can be derived from plants or animals, but many more are not associated in any way with organisms. Not all organic compounds can be produced by synthesis, and we still depend upon plants and animals for some of the most important — starch, sugar, fats, casein, gelatin, albumen, cellulose, and many others. The total number of compounds of carbon produced in the laboratory or from natural sources probably exceeds 400,000.

The existence of this vast number of compounds of carbon is explained by the capacity of its atoms to share electrons with many other kinds of atoms and, especially, by the capacity of two carbon atoms to form a stable bond by sharing electrons with each other. Since carbon has four valence electrons per atom, the maximum valence number of the element is 4. The carbon atom may share all four electrons and thus may be linked to four univalent atoms, such as hydrogen or chlorine. Two carbon atoms may share one, two, or three pairs of electrons with each other, thus producing single, double, or triple bonds between them. When the other electrons of the carbon atoms are shared with hydrogen, we have compounds known as hydrocarbons.

TABLE 32
The Hydrocarbons

Methane Series C_nH_{2n+2}	Ethylene Series C_nH_{2n}	Acetylene Series C_nH_{2n-2}	Benzene Series C_nH_{2n-6}
Methane CH_4	Ethylene (Ethene) C_2H_4	Acetylene (Ethyne) C_2H_2	Benzene C_6H_6
Ethane C_2H_6	Propylene C_3H_6	Propine C_3H_4	Toluene C_7H_8
Propane C_3H_8	Butylene C_4H_8	Butine C_4H_6	Xylene C_8H_{10}
Butane C_4H_{10}	Pentylene C_5H_{10}	Pentine C_5H_8	
Pentane C_5H_{12}	Hexylene C_6H_{12}		
Hexane C_6H_{14}	Heptylene C_7H_{14}		
Heptane C_7H_{16}	Octylene C_8H_{16}		
Octane C_8H_{18}			
Nonane C_9H_{20}			
Decane $C_{10}H_{22}$			

2 The Hydrocarbons

A hydrocarbon, as indicated in the preceding paragraph, is a compound of carbon and hydrogen. There is a large number of these compounds, but, fortunately, most of them can be classified as members of one of four series. The first members of these series are shown in Table 32. Each group is called a *homologous series*. Each hydrocarbon in a series differs from the preceding member of its series by containing one more carbon atom and two more hydrogen atoms (CH_2) per molecule. The members of each series have the same general formula and display the same general chemical behavior, although certain differences in properties accompany increasing size of the molecules, as might be expected.

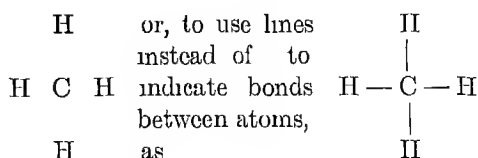
3. The Methane Series

These hydrocarbons are found in petroleum and its products — gasoline, kerosene, lubricating oils, and paraffin. *Methane* is the principal component of natural gas. Because solid members of the series are

found in paraffin, these substances are sometimes called the paraffin hydrocarbons. They are also called saturated hydrocarbons, because each of the valence bonds of carbon consists of a single pair of electrons, which unites a carbon atom with hydrogen or with another atom of carbon. The first four hydrocarbons of the methane series are gases at ordinary temperature. Methane boils at about -161° , and butane at about -0.6° . The members from C_5H_{12} to $C_{15}H_{32}$ are liquids, and those above $C_{15}H_{32}$ are solids.

4. Structural Formulas

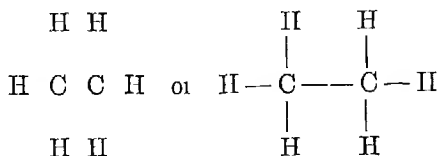
The structure of a molecule of methane can be represented, in two dimensions, as



If we attempted to represent the molecule in three-dimensional space, we should place the carbon atom in the center of a tetra-

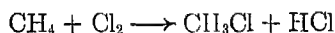
hedron with the four atoms of hydrogen at the corners

In ethane, two carbon atoms are joined to each other; this link replaces one bond of each carbon atom with hydrogen

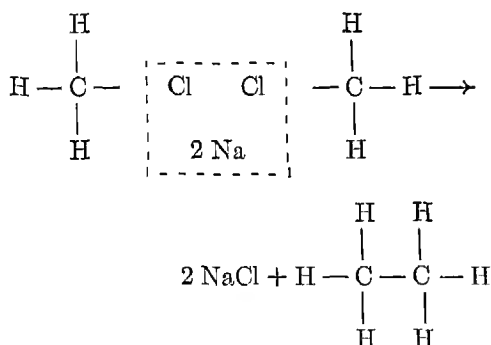


Methane may be converted into ethane in the following manner

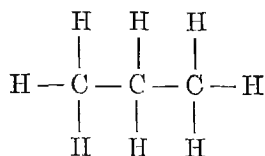
(1) Methane reacts with chlorine to form methyl chloride



(2) Metallic sodium then reacts with two molecules of methyl chloride, removing the chlorine atoms to form sodium chloride and allowing two methyl groups (CH_3) to combine



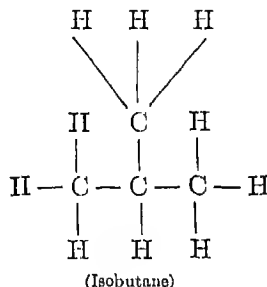
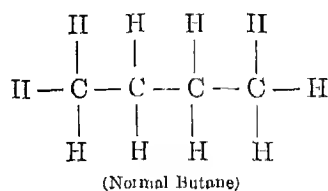
The other members of the series are similar to methane and ethane, but differ in having longer, and sometimes branched, chains of carbon atoms. In *propane* three carbon atoms are joined together in the form of a chain



The formulas of these compounds are usually written as CH_4 , $\text{CH}_3 - \text{CH}_3$, and $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$

5 Isomers Having Different Structures

For none of the first three hydrocarbons of the methane series is it possible to construct formulas showing linkages between the atoms that are different from those given. But for butane, it is possible to write formulas for two arrangements

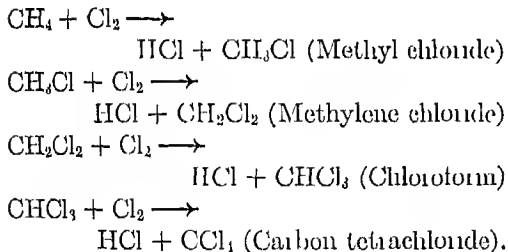


These two formulas represent two different substances which have the same empirical formula, C_4H_{10} . *Isobutane* is called an *isomer* of *normal butane*. It is apparent that the difference in structure lies in the linkage of one carbon atom with three others in isobutane and with two in normal butane. We say that the carbon chain is branched in isobutane. There are three isomers of *pentane*, and with an increasing number of carbon atoms in the molecule, the number of possible isomers soon reaches an enormous value. The formation of a substance with different properties with each change in structural arrangement, together with the ability of carbon atoms to join together to make chains and even rings, accounts for the vast number of carbon compounds which can be

prepared or are known to exist. The possibilities are almost unlimited.

6 Properties of the Methane Hydrocarbons

The members of the methane series are colorless gases, liquids, or solids. They are insoluble in water. They burn in the presence of oxygen to form water and carbon dioxide. They are relatively inactive substances, the name paraffin, *par(um) affinitas*, means "little affinity." They are not affected, or only slightly affected, by strong acids, bases, and most oxidizing agents. Their activity decreases with increasing molecular weight, so that the heavier members are to be classified as very nearly inert substances. The higher members will react with chlorine, in bright sunlight, to form compounds in which chlorine both replaces hydrogen in the linkage with carbon and combines with it to form hydrogen chloride.

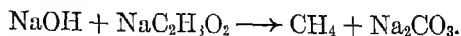


Since the methane hydrocarbons are saturated, they can react with chlorine, or other elements, only in reactions of this kind. These are called *substitution* reactions.

7 Methane

Methane is sometimes called *marsh gas*. This name refers to its production during the decay of vegetable matter in swamps, marshes, and ponds; it is produced whenever the decomposition of organic matter occurs in the absence of air. It is present in the gases that escape during the distillation of coal and wood. In the laboratory it is produced by heating, out of contact with air,

a mixture of sodium acetate and sodium hydroxide

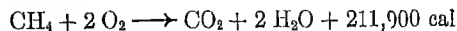


There is usually a small amount of methane in solution in petroleum, and natural gas from some wells contains from 80 to 95 per cent of methane. A mixture of methane and air, called *fire damp*, is a source of considerable danger in coal mines, because of its inflammability.

8 Natural Gas

Natural gas is often encountered in drilling wells for petroleum and sometimes is found where petroleum is not present. It is found in folds of rock strata, where it has been trapped in the top of the fold by collections of water and oil below. The folds are called *anticlines*. The gas is usually under great pressure. The principal producing localities of the United States are in Pennsylvania, West Virginia, Oklahoma, Louisiana, Kansas, Texas, Ohio, Indiana, Kentucky, and California. The percentage of methane varies considerably in the natural gas from these regions. Some of the gas produced in Texas contains about 50 per cent of methane and 38 per cent of nitrogen. That from Pennsylvania and West Virginia averages about 80 per cent of methane, and the natural gas of Ohio and Indiana contains about 94 per cent of this hydrocarbon.

Natural gas is a valuable fuel, since it usually contains a very high percentage of methane, which has a high heat of combustion.



It is forced through pipe lines to cities which are several hundred miles from the source. A considerable quantity is also used in the production of "carbon black" (page 293). Since it often escapes with the petroleum from oil wells, an enormous portion of our natural gas resources has been wasted. The annual production in the United States is in

excess of two and one-half trillion cubic feet. Most natural gas contains some carbon dioxide and nitrogen, "wind gas" contains enough of these two substances to prevent combustion.

PETROLEUM AND ITS PRODUCTS

9. Petroleum

Petroleum is a solution of gaseous and solid hydrocarbons in a mixture of liquid hydrocarbons. Most, but not all, of these hydrocarbons belong to the methane series. Petroleum is found in certain geological formations, such as anticlines or folds, at depths that vary from a few feet to two miles. The oil-bearing strata of rock or sand is reached by wells, from which the oil is pumped. The name petroleum is derived from two words, *petra oleum*, meaning rock or mineral oil. The crude oil and the products obtained from it are sometimes called mineral oils to distinguish them from vegetable and animal oils, which have an entirely different composition and possess different chemical properties (page 588).

The United States produces normally about 65-70 per cent of the petroleum supply of the world. The remaining 30-35 per cent is distributed among several countries, of which Venezuela, Russia, Persia, Rumania, Dutch East Indies, and Mexico are the most important producers. The first oil well in America was drilled at Titusville, Pennsylvania, in 1859. Previous to that time oil had been observed on the surface of the water of some of the streams of this region, and some of it had been collected and sold as a medicine, *Nature's Remedy*. It was also known to the Indians, who probably used it to some extent as a medicinal agent. The principal oil-producing states of this country, at the present time, are California, Oklahoma, and Texas, with smaller fields in Kansas, Louisiana, Arkansas, New Mexico, Pennsylvania, and several other states. The world's production of petroleum is normally around 2,000,000,000 barrels of 42 gallons each. The United States produces about 1,500,-

000,000 barrels, and of this quantity the production of Texas, California, and Oklahoma comprises about three fourths.

The petroleum from different parts of the world varies widely as to the nature of the hydrocarbons that it contains. The petroleum of Pennsylvania consists almost entirely of hydrocarbons of the methane series, and the residue left after distillation is largely solid paraffin. Petroleum from California gives a residue of asphalt and is called an "asphalt base oil" to distinguish it from the "paraffin base oils" of the eastern United States. Petroleum from California, Russia, Borneo, and Java also contains variable amounts of the benzene hydrocarbons. Petroleum usually contains small amounts of sulfur compounds, which are objectionable when they appear in the products obtained from the crude oil refinery. The removal of these compounds increases considerably the cost of petroleum refining.

10. The Refining of Petroleum

To obtain the products listed on page 564, petroleum is fractionally distilled. A diagram of the old-fashioned refinery, which shows the principles involved, is shown in Figure 257. Modern practice uses the "bubble tower" to separate the oil into its different fractions (Figure 258). Petroleum under pressure is first heated by being passed through pipes in a furnace. The hot liquid is then passed into a "flash chamber" where, by a reduction of the pressure, it is converted into vapors. Some of the heavier portions of the oil do not vaporize and these are separated from other fractions at this point. The vapors then pass into the "bubble tower," which consists of a great many sections, or pans, placed one above the other. As the vapors pass upward, the higher boiling oils condense and the gases are then made to bubble up through these liquids as they pass from one section to the next. The gasoline vapors pass through the tower and are then condensed by cooling. Kerosene is condensed in the upper portion of the tower,

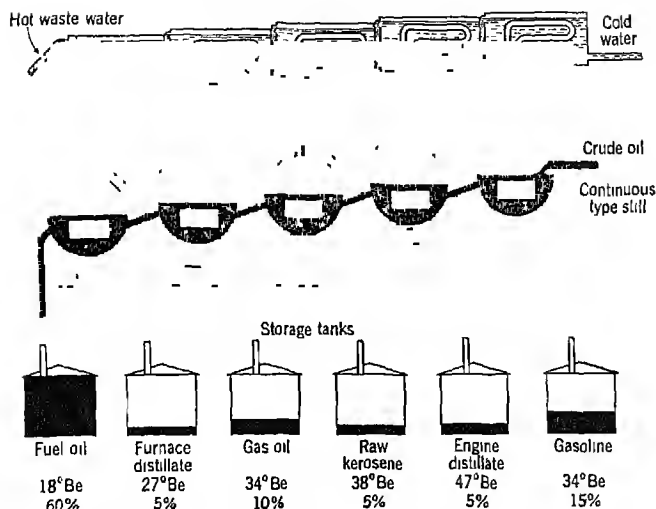


Figure 257. Diagram Showing the Fractional Distillation of Petroleum

The fuel oil can be further distilled with steam to give lubricating oils. Degrees Be refer to the densities of the different products.

gas oil in the middle, and the heavier oils at the bottom. The heavier hydrocarbon fractions may be distilled by use of superheated steam. The fraction containing the lubricating oils is again distilled with steam and is

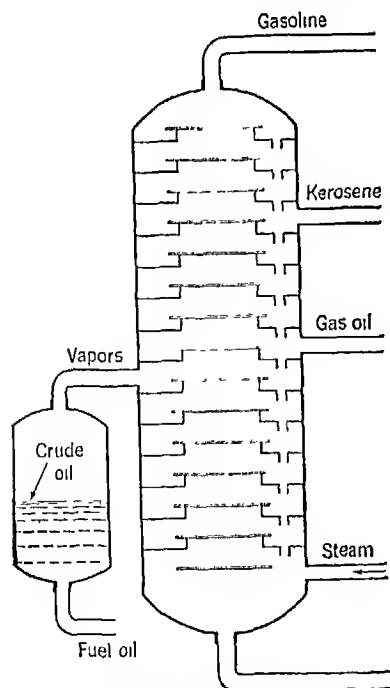


Figure 258. Bubble Tower

divided into several portions — light, medium, and heavy motor oils. The paraffin is removed from these oils by chilling them. The oils are usually filtered through Fuller's earth to remove some of the colored compounds that they contain. The products of the petroleum refinery are usually treated with sulfuric acid to remove objectionable impurities, especially compounds of sulfur. The acid is heavier than the oils and settles to the bottom of the treating tanks, where it is drawn off. The oils are then washed with a solution of sodium hydroxide or sodium carbonate in order to neutralize the acid. Recently, waxes, gums, asphalt, and other substances found especially in motor oils have been removed by the use of solvents such as liquid sulfur dioxide. This procedure is said to give lubricating oils that have constant viscosity and do not form deposits of wax, gum, or carbon. Sulfur compounds are now removed by using a solution of litharge, PbO , in sodium hydroxide. However, the refineries still use sulfuric acid in enormous quantities.

A residue of tar, or of coke if carbonization is complete, is left after the complete distillation and removal of all the oil fractions.

TABLE 33
Petroleum Products

Product	Composition	Boiling Point	Uses
Gases	Methane-butane		Fuel, manufacture of carbon black
Petroleum ether	Pentane-heptane	35°–90°	Solvent, dry-cleaning
Gasoline	Hexane-nonane	up to 200°	Fuel, solvent
Kerosene	Decane-hexadecane	200°–300°	Illumination, fuel oil
Gas oil		up to 375°	Cracked to give gasoline, fuel for oil-burning furnaces, enrichment of water gas
Lubricating oil	$C_{20}H_{42}$ up	300° up	Lubrication
Vaseline		semi-solid	Lubrication
Paraffin		melting point about 55°	Candles, water-proofing
Tar			Artificial asphalt
Petroleum coke			Fuel, electrodes

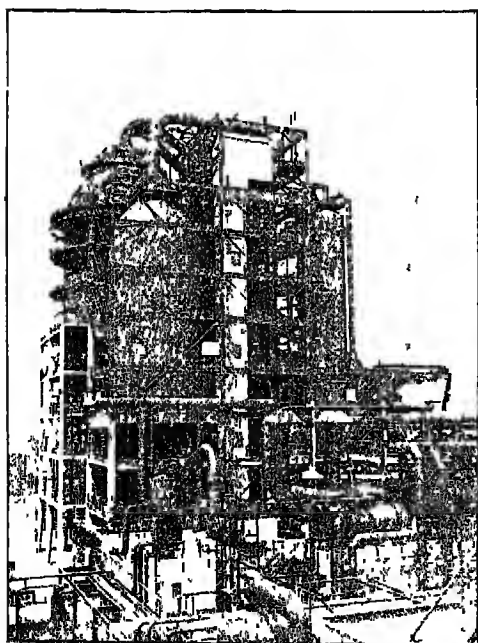
The tar is used in making roofing, sidewalks, and roads. Coke is used as a fuel, in metallurgy, and in the manufacture of electrodes.

11 Gasoline

Gasoline is a mixture of low-boiling petroleum hydrocarbons, such as hexane, heptane, octane, and nonane. With more than

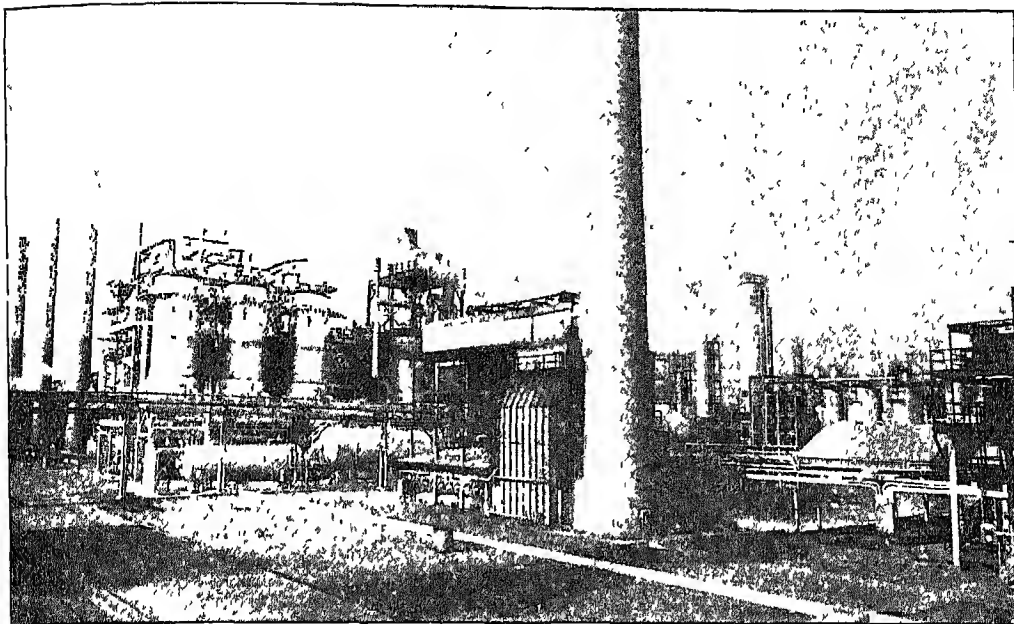
30,000,000 automobiles to provide with fuel, as well as airplanes and other internal combustion engines, the production of gasoline has become one of the largest industries in the country; in 1940, this production was 206,000,000,000 gallons. Ordinarily, the gasoline fraction of petroleum amounts to about 20 per cent of the crude oil, but this has been increased to almost 44 per cent by modifications of refinery practice. In the past quarter of a century, the production of gasoline has kept pace with the increase in the number of automobiles, both have increased almost 600 per cent, but the production of petroleum has increased only 200 per cent during the same period.

Much of the increase in the production of gasoline has been accomplished through the use of a process called *cracking*, by which some of the heavier and less volatile hydrocarbons are broken up into lighter compounds that boil at lower temperatures. The original cracking process was developed by Burton in 1913. There are many processes now in use. The decomposition of the heavier hydrocarbons is brought about by heating oil under pressure or by passing the hot oil-vapors over catalysts, such as anhydrous aluminum chloride. Many different catalysts and different methods of bringing them into contact with the hydrocarbons are



Courtesy of Gulf Oil Corporation

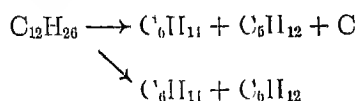
Figure 259 Fluid Catalytic Cracker



Courtesy of Sun Oil Company

Figure 260 A Large Houdry Catalytic Cracking Unit

in use. Finely divided catalysts are now utilized rather extensively. These are mixed as a powder with the vapors of hydrocarbons. A typical cracking reaction is shown by the following equation:



After the cracking treatment the oil is passed into a flash chamber from which the vapors enter the "bubble tower." Cracking also produces lighter, lower boiling hydrocarbons that are valuable as fuel for airplane engines.

The demand for gasoline has also been supplied by the recovery of the vapors of low-boiling hydrocarbons from natural gas, which is often saturated with the vapors of such substances, chiefly C_5H_{12} , C_6H_{14} , and C_7H_{16} . They are separated from methane, the principal constituent of natural gas, by the use of activated charcoal, which adsorbs the less volatile portions of the gas more readily than it adsorbs methane, by washing

the gas with oil in which the gasoline-hydrocarbons are soluble, or by subjecting the gas to pressure and a low temperature, which liquefies those hydrocarbons that can be used as gasoline. About one tenth of the gasoline produced in the United States is obtained from this source. It is called *casing head gasoline*.

The gasoline produced by cracking processes is often blended with casing head gasoline. The former usually contains less volatile and the latter more volatile hydrocarbons than the "straight-run" gasoline produced by the straight distillation of petroleum.

The present tendency in the industry is in the direction of gasoline containing a single, or at most three or four, hydrocarbons. Such gasolines allow the combustion in automotive engines to be controlled more accurately than is possible with more complex mixtures.

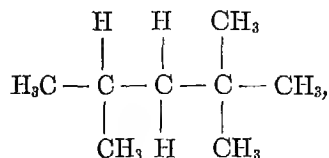
12 Anti-Knock Gasolines

The power obtainable by exploding a mixture of air and gasoline vapor in the cylinders

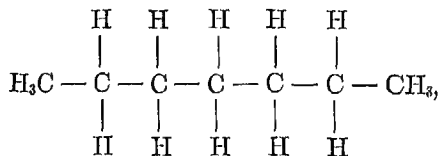
of an automobile engine depends upon the expansion that occurs at the time of the explosion. If the mixture of gases is compressed before the explosion, more power should therefore be produced. Automobile engineers have made use of this principle in developing the high compression motors that are now widely used. The immediate and practical result is an increase in the mileage per gallon of fuel, but with ordinary gasoline, these high compression motors cannot operate without a rather serious "fuel knock." This knock is produced by a very sudden and complete explosion, which produces a sudden shove against the piston head of the cylinder. To prevent knocking, the explosion must occur more or less as a wave and must develop a slower "push" against the head of the piston. Straight-run gasoline causes the engine to "knock" badly. Gasolines produced by cracking are said to be less objectionable, but most of the gasoline used today is a mixture or blend of hydrocarbons obtained from different sources or in different ways—straight distillation, cracking, natural gas, and so on. These blends are compounded in proportions designed to secure the most satisfactory anti-knock properties. Ordinary distilled gasoline, which produces pronounced knock, contains hydrocarbons consisting of straight chains of carbon atoms, that is, normal hydrocarbons such as normal heptane. The cracked gasoline contains hydrocarbons consisting of branched chains of carbon atoms—for example, iso-heptane and iso-octane (page 560)—which do not cause much if any knock. Benzene is also added to some of the blends to decrease the knock produced by the fuel. The most familiar anti-knock gasoline, however, is that which contains small quantities of lead tetraethyl, ethylene dichloride, and ethylene dibromide, $\text{Pb}(\text{C}_2\text{H}_5)_4$, $\text{C}_2\text{H}_4\text{Cl}_2$, and $\text{C}_2\text{H}_4\text{Br}_2$. The halogen compounds are added to form volatile compounds of lead so that this element is removed from the cylinders along with other products of combustion.

13. Anti-Knock Rating of Gasoline

The rating of a gasoline with regard to its tendency to produce knocking is called the *octane number*. Pure iso-octane,



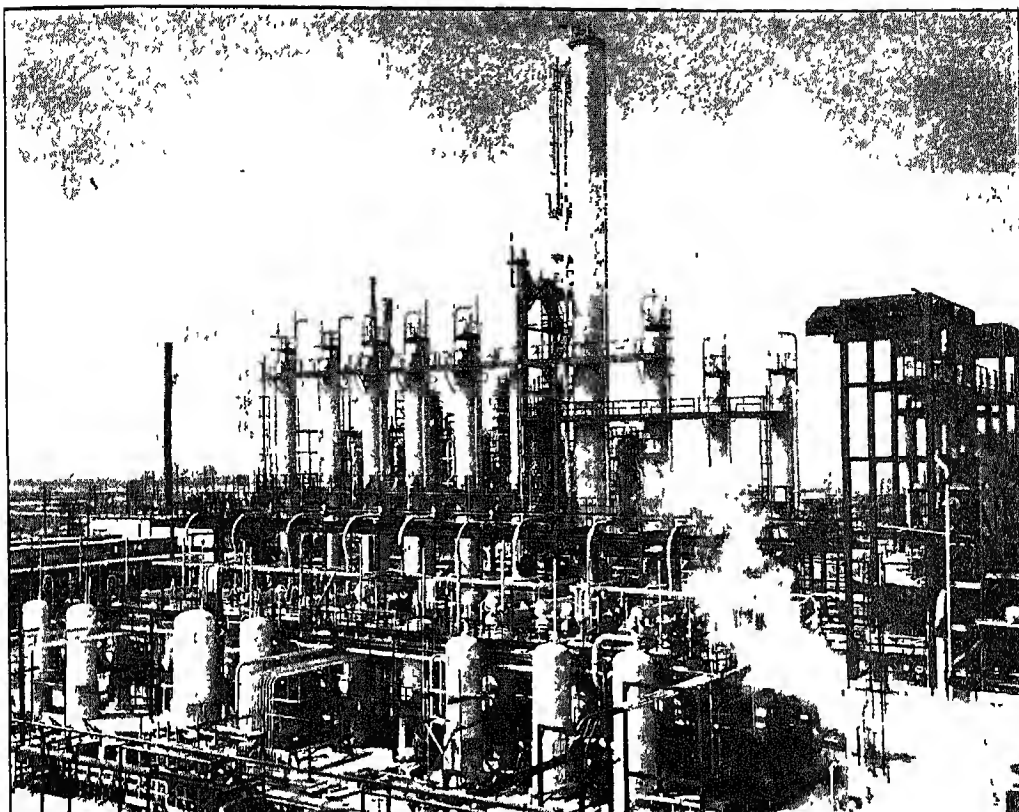
is given an octane number of 100, because it produces little or no knocking as compared with ordinary, straight-run gasoline. Normal heptane,



produces a very pronounced knock and is given the octane number of 0. To determine the rating of a certain fuel, the gasoline is used in a standard engine and its tendency to produce knocking is compared with different mixtures of the two hydrocarbons named above. If the gasoline produces the same intensity of knocking as a mixture containing 80 per cent of iso-octane, its octane number is 80.

14. Polymerization

During recent years polymerized gasoline has also entered the field. As the name indicates, this process involves the building up of heavier molecules from lighter ones by polymerization. Hydrocarbons, both saturated and unsaturated, of low molecular weight and produced by cracking or by the distillation of petroleum, are heated to 500°–600° under high pressure and in the presence of suitable catalysts. As a result of this treatment the saturated hydrocarbons lose hydrogen and are converted into unsaturated compounds. The unsaturated hydrocarbons polymerize to form other hydrocarbons, many of which are suitable for use as gaso-

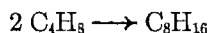


Courtesy of Gulf Oil Corporation

Figure 261 An Alkylation Plant

Alkylates are petroleum chemicals used to step up the anti-knock rating of aviation gasoline. This plant has contributed greatly to the production of 100 octane gasoline for military purposes.

line. For example, butylene may polymerize to form a dibutylene



15 Re-forming

In this process hydrocarbons composed, for the most part, of molecules in which the carbon atoms are arranged in straight chains, are cracked. The products vary greatly. Among them are found unsaturated hydrocarbons which result from the liberation of hydrogen from some of the molecules; branched-chain hydrocarbons such as isobutane and isopentane, and aromatic hydrocarbons such as toluene, $\text{C}_6\text{H}_5\text{CH}_3$. This was an important source of the toluene used to produce the trinitrotoluene (TNT) used

in the recent war. The unsaturated and branched-chain hydrocarbons produced in this process are generally more desirable components of gasoline than the original saturated straight chain compounds.

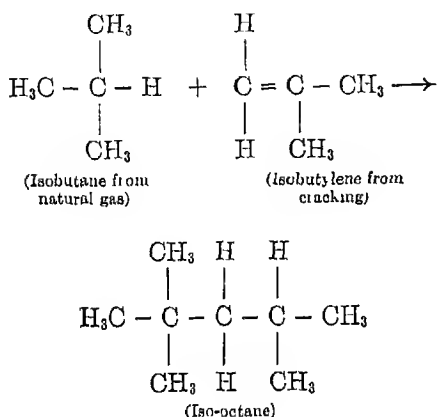
16 Hydrogenation of Petroleum

By a process developed first in Germany and later employed in this country and elsewhere, crude petroleum is hydrogenated by treatment with hydrogen (in the presence of catalysts) under about 200 atmospheres of pressure. The distillation of the hydrogenated oil yields much larger quantities of the gasoline-hydrocarbons than can be obtained from untreated, crude petroleum. The heavy residues remaining after the more volatile compounds of petroleum have been

removed by fractional distillation can also be hydrogenated in a similar manner to produce gasoline

17 Alkylation

Another process used in the gasoline industry is called *alkylation*. In this process saturated hydrocarbons, such as isobutane, react with unsaturated hydrocarbons, such as isobutylene, to form hydrocarbons that are composed of branched chain molecules

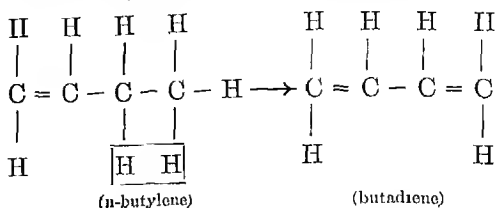


Iso-octane is a liquid hydrocarbon that was widely used during World War II as a high-grade aviation gasoline. The reaction by which it is made is catalyzed by hydrogen fluoride.

18. Butadiene

During cracking operations, many different unsaturated hydrocarbons, such as ethylene and propylene, are produced. These substances are of value as starting materials for use in the synthesis of many organic compounds. One of the gaseous products of cracking is an unsaturated hydrocarbon of the ethylene series called *normal butylene*. This compound can be converted, by a catalyzed reaction in which hydrogen is removed from the molecule, into the still further unsaturated hydrocarbon, *butadiene*. This compound is extensively used in the manufacture of Buna S, the synthetic rubber

(page 610) most extensively produced and used during and since World War II



19 Motor Problems of the Future

The tremendous rate at which we are now consuming our petroleum resources causes one to look ahead to the time when these supplies of gasoline and kerosene will have been exhausted. This time will not come soon, but since the supply is a natural resource that is not being replenished, it cannot last forever. Sooner or later our civilization must find new sources of these fuels or entirely different kinds of fuels that can be used for the same purposes.

The Bergius process for the hydrogenation of coal has made available one more source of gasoline and lubricating oils (page 117). This process depends upon the reaction of finely powdered coal, mixed with oil, and hydrogen. The reaction is made to occur at about 500°, under high pressures, and in the presence of a catalyst. The oil thus produced is fractionally distilled to give many of the products now obtained from petroleum. These include gasoline, kerosene, and various grades of lubricating oils. But like petroleum itself, the coal used in the Bergius process is also a natural resource and cannot serve as an everlasting source of liquid fuels. The oils obtainable from this source, however, may augment considerably the supplies produced from petroleum, as the latter begin to dwindle.

A more promising source of motor fuel is the conversion of carbon monoxide into hydrocarbons by the *Fischer-Tropsch Process*. In this process, water gas, which contains both carbon monoxide and hydrogen (page 111), is passed over a catalyst (iron and nickel) at about 200°. Saturated straight-chain hydrocarbons are produced. These compounds can be converted by reforming (page 567) into unsaturated and branched-chain hydrocarbons which give gasoline of excellent anti-knock quality. The carbon monoxide and hydrogen used in this process can also be produced by a reaction of methane with steam.

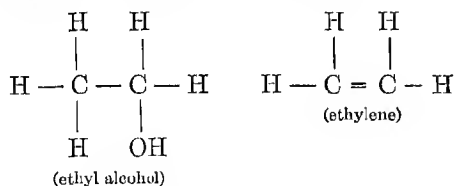
The most likely source of petroleum products

of the distant future is oil shale. Certain shales of many of the western and some of the central states of the United States, as well as shales in other parts of the world, contain organic compounds. The shales do not contain petroleum, but when they are distilled in the absence of air, an oil resembling petroleum is obtained. One ton of shale yields about one barrel of this oil. When the oil is fractionally distilled, the products obtained include gasoline, kerosene, lubricating oils, and similar substances. The distillation of the shale also yields ammonia, which can be converted into ammonium sulfate for use as a fertilizer. At the present time the distillation of shale is not a practical method of obtaining petroleum products, because the expense involved prevents the process from competing successfully with the petroleum refinery.

UNSATURATED HYDROCARBONS

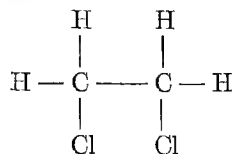
20. The Ethylene Series

Ethylene is the most important member of this series of hydrocarbons. The structure of its molecule can be explained most readily through a description of a method by which the substance can be produced. Ethyl alcohol (C_2H_5OH) is treated with concentrated sulfuric acid, or alcohol vapor is passed over anhydrous aluminum silicate. A molecule of water is removed from the alcohol, and the gas — ethylene — is produced.



The removal of a hydrogen atom from one carbon atom and the removal of the hydroxyl radical from the other leaves each carbon atom with one unused valence. To show that carbon has a valence of four, the organic chemist places this unused bond between the two carbon atoms, which are then said to be united by a *double bond*. Compounds containing double bonds are *unsaturated*. This means that the molecule will add on atoms of active elements, such as chlorine and bromine. Thus, two atoms of

chlorine will combine with a molecule of ethylene to form

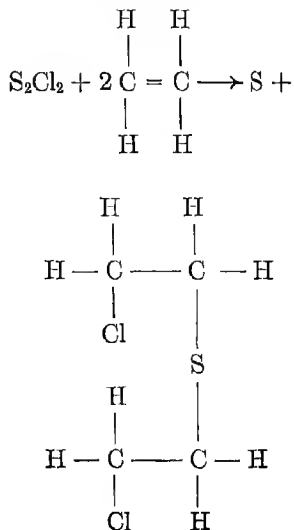


dichloroethane. The unsaturated hydrocarbons also react, as methane does, with chlorine and other active elements to form substitution compounds, in which chlorine replaces hydrogen.

The unsaturated hydrocarbons are more readily decomposed by heat than the saturated hydrocarbons. When a gaseous mixture containing the former is burned, the flame is made luminous by particles of carbon produced by the decomposition. The flame of a gaseous mixture of the saturated hydrocarbons is nearly colorless. In the latter, the hydrocarbons are converted directly in the flame into carbon dioxide and water, while unsaturated hydrocarbons decompose, at least partially, to form some particles of free carbon. These particles soon completely burn if an excess of oxygen is available. If the supply of oxygen is insufficient for their combustion, the particles of carbon escape from the flame as black smoke.

21 The Uses of Ethylene

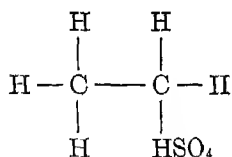
Ethylene has many interesting uses. For example, it reacts with sulfur monochloride to form mustard gas (page 336).



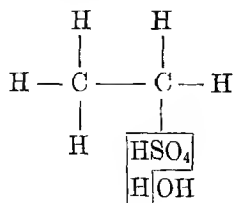
An ethylene-oxygen mixture is used as an anesthetic in general surgical practice. It is said to have decided advantages over ether. The patient recovers consciousness much sooner; the anesthetic acts quickly, and there is no irritation of the lungs, a condition which sometimes causes pneumonia after the inhalation of ether to produce anesthesia. A few disasters, resulting from the chance ignition of the very explosive ethylene-oxygen mixture that must be used, have marred the record of this anesthetic.

Ethylene is also used to hasten the ripening of citrus and certain other fruits, or at least to give them the color of ripened fruit when they must be picked and shipped to markets while they are still in the unripened, green-colored state. Either during transit to market or upon arrival, the fruit is exposed to an atmosphere containing a small amount of ethylene. Its use is also said to increase the sugar content, but not the vitamin content, of the unripened fruit. It may also be used to shorten the dormant period through which potatoes and other tubers must pass before they are ready to start growing again.

If ethylene is treated with sulfuric acid, the two substances react to form an addition compound



This substance is then allowed to hydrolyze, and a sulfonic acid molecule is formed, leaving a molecule of ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$

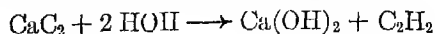


This reaction is used commercially to produce ethyl alcohol. It is typical of a number of reactions, similar in nature, but involving other unsaturated hydrocarbons,

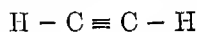
that can be used to produce some of the higher alcohols not readily produced by other means.

22 The Acetylene Series

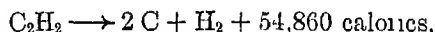
The only important member of this series is acetylene, C_2H_2 , which is produced by allowing water to react with calcium carbide (page 311). The reaction is as follows:



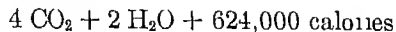
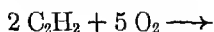
This reaction is typical of those used to produce the hydrogen compounds of the non-metals. Compare, in this connection, the production of ammonia from Mg_3N_2 and of phosphine from Ca_3P_2 . Structurally, the acetylene molecule differs from the molecules of ethane and ethylene in possessing a *triple bond*, or two additional pairs of electrons between its carbon atoms:



Pure acetylene is almost odorless, is poisonous, burns with a yellow smoky flame, and forms addition compounds with chlorine and other active elements. The gas is unstable, as might be expected from its heat of formation:



It burns with an extremely hot flame, because to the quantity of heat liberated as indicated by this equation there is added the heat produced in the formation of carbon dioxide and water:

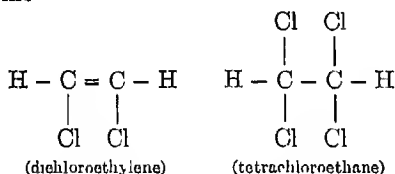


When it is compressed it is likely to explode violently. For this reason liquefied or compressed acetylene is not used for lighting purposes. It is a good illuminant, however, because of its highly unsaturated nature. When used for this purpose it is usually dissolved under pressure in acetone, in which it is very soluble. The solution is stored in cylinders and used, where electrical lighting is not available, as a source of illuminating gas. In the days before the

"self-starter" and the storage battery equipment of automobiles were widely adopted, lighting was provided by cylinders containing an acetylene-acetone solution. At the present time, acetylene is used for lighting on farms and in isolated communities, and for producing flood lights where electricity is unavailable. The oxyacetylene blowpipe is used to produce high temperatures in the welding and cutting of metals. Acetylene has also been used as an anesthetic.

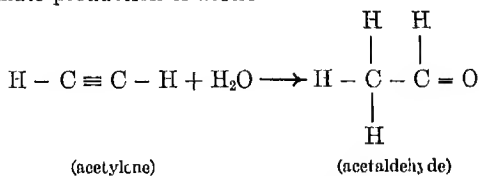
23 Organic Syntheses Based upon Acetylene

The addition compounds formed by acetylene are represented by the following products with chlorine:

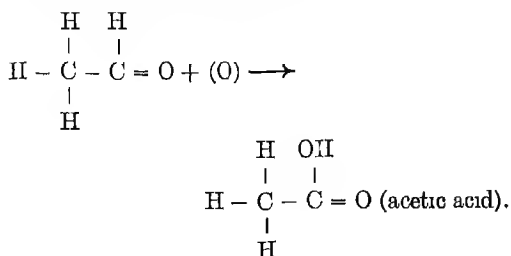


The first of these two compounds is of some importance as a fumigant, in dry cleaning, and as a solvent in the extraction of vegetable oils. It is non-poisonous and non-explosive when mixed with air.

Because of its unsaturated character, acetylene is the starting material in the production of many synthetic organic compounds. One of the most important of these reactions involves the ultimate production of acetic acid:

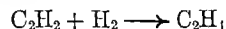


This reaction occurs in the presence of mercury salts, which act as catalysts. The acetaldehyde is then oxidized to acetic acid:



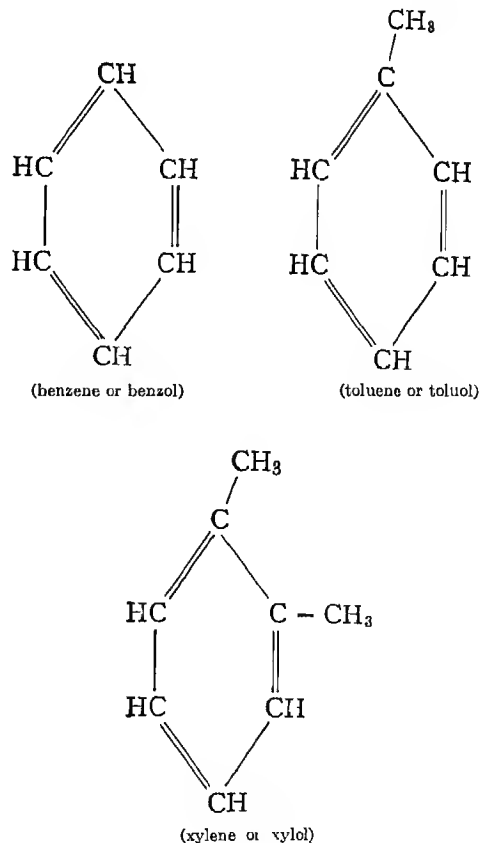
This reaction is also catalyzed, usually by vanadium or cerium oxide.

Acetylene is also converted catalytically into ethylene by causing hydrogen to add on to the two carbon atoms:



24 The Benzene Series and Related Hydrocarbons

Among the many valuable substances recovered from coal gas and from coal tar — both of which are products of the destructive distillation of coal — are certain hydrocarbons which differ greatly from the hydrocarbons found in petroleum and natural gas. Among these are the three most prominent and important members of the benzene series: benzene, toluene, and xylene. The structural formulas of these hydrocarbons are shown below:



The chemical properties of these substances show that they are unsaturated. It will be noticed that three double bonds are placed in each molecule. This arrangement permits each carbon atom to be displayed as having its normal valence (four). We are not to think, however, of the benzene hydrocarbons as showing the same tendency as ethylene, for example, to form addition compounds. Instead, they are only slightly active in this respect. They form substitution compounds more readily. The ring structure, shown above, is based largely upon the chemical properties of these substances. This structure will be discussed further in another chapter (page 593). These hydrocarbons are used as solvents, they are used in the manufacture of dyes, drugs, and explosives, and benzene finds some use as a motor fuel. Because of the odors of some of them, or the odors of materials from which they are produced, they are sometimes called the *aromatic hydrocarbons*.

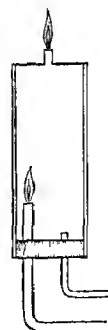
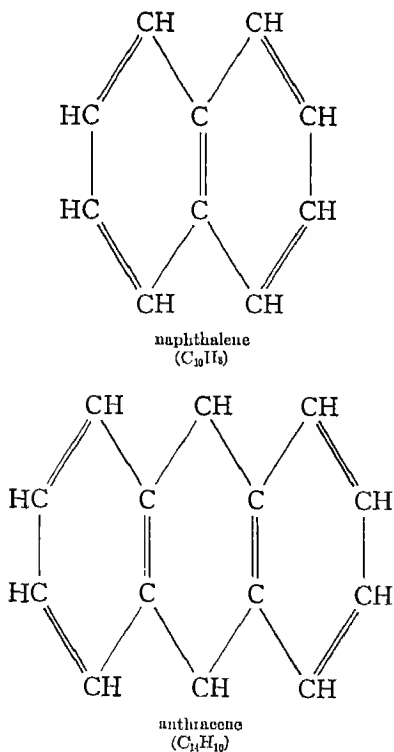


Figure 262. The Burning of a Gas in Air and the Burning of Air in a Gas

The lower flame is caused by the reaction between the gas which fills the large tube and the air which is drawn into the tube through the opening at the bottom. The upper flame is caused by the combustion of the gas in the air.

Coal tar is also the source of two other hydrocarbons of great importance — naphthalene and anthracene. These substances are related to benzene, but they differ from it in the complexity of their ring structures. These hydrocarbons are also unsaturated. Naphthalene is used as moth-balls, in the enriching of gas, and in the manufacture of dyes, such as indigo, and of many other valuable organic compounds. Anthracene is used in making dyes, particularly some of the important red dyes.

ILLUMINATING AND FUEL GAS

25. Gas Flames

The heat liberated during combustion may heat the solid products of combustion, or the burning substance itself, to incandescence. When this happens the reaction is accompanied by light. When charcoal or coke burns, the solid becomes white-hot and emits light, but there is little or no flame. The flames which accompany the burning of coal, oil, or a candle are the result of the combustion of gases that are vaporized from the combustible substance by the heat of the reaction. These flames are luminous, if carbon compounds in the gases are decomposed to form small particles of solid carbon (page 569).

Ordinarily, we think of a stream of gas as burn-

ing in air. This is because we store up the gas and ignite it at the outlet of a small tube or burner, where it comes into contact with the air. We might secure the same result if we stored up air and ignited a small stream of it as it escaped into an atmosphere of gas. We might then think of air as burning in gas. Combustion is really a chemical reaction between two substances, and although we usually speak of one substance as supporting the combustion of the other, this practice is only a convention. Figure 262 illustrates a method by which the burning of air in an atmosphere of gas can be demonstrated.

26 The Structure of Flames

Simple flames, consisting of two cones, one within the other, are produced when one gas burns by combining with another (Figure 263). Such flames are produced, with the ordinary Bunsen burner, when hydrogen or carbon monoxide burns in the air, or when hydrogen burns in chlorine. Combustion occurs only in the outer cone. The inner cone consists of uncombined gases.

If the gas contains hydrocarbons, a more complex flame (Figure 233) is produced. If the openings at the bottom of the burner are closed, the gas must burn in air, drawing

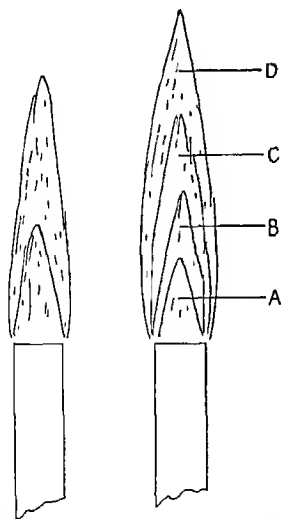


Figure 263 Simple and Complex Flames

The flame on the left is produced when one gas burns by directly combining with another. The flame on the right is produced by burning hydrocarbons.

from the surroundings the oxygen needed for the reaction. Under these conditions, the hydrocarbons in the interior of the flame are heated, but there is no oxygen to cause their combustion. The molecules are consequently decomposed (cracked), and particles of carbon that are liberated make the flame luminous. If the openings at the bottom of the burner are opened, air is mixed there with the gas, and a flame such as that shown in Figure 263 results.

The different cones of a flame are caused by the different reactions that occur in them. In Figure 263, cone (A) contains unchanged gases. The temperature in this region is low, a match suspended in the mouth of the Bunsen burner, before the burner is lighted, is not ignited by the burning gas. The combustion begins in cone (B). The reaction in this cone results in the formation of hydrogen and carbon monoxide. Cone (B) is bluish-green in color, if the air supply is properly regulated. If too much air is admitted, this cone "strikes back" — that is, travels down the barrel of the burner and causes the gas to ignite at the base. In cone (C) hydrogen and carbon monoxide are partially converted into water and carbon dioxide. Sufficient heat is liberated in this region to crack some of the unchanged hydrocarbon molecules (especially acetylene and ethylene), thus producing small particles of carbon, which make this cone luminous. The hottest part of the flame is just below the tip of this cone. The particles of carbon are completely burned, however, in cone (C), hence cone (D) is not luminous. In cone (D) the combustion of hydrogen and carbon monoxide is completed. This cone is most apparent as a blue, almost invisible region, near the base of the flame, since the luminous region of cone (C) obscures it in the upper portion of the flame.

The luminosity of a flame depends upon several factors: the air supply, the pressure of the gas, the temperature of the burner tube, the gas, and the air, and the presence of inert gases. In some flames, a portion of the energy of the reaction is released as light, and the flames are luminous, although no solid particles are present. This happens, for example, in the burning of ammonia.

The temperature attained in the flame of a Bunsen burner varies under optimum conditions from 300° near the base of the flame to about 1500° just above cone (C). That portion of the flame which contains hydrogen and carbon monoxide (cone B) is sometimes called the *reducing flame*, because these substances act as reducing agents. The upper portion of the flame, in which there is an abundant supply of oxygen, is called the *oxidizing flame*.

27. Gas Mantles

Water gas (H_2 and CO), and also natural gas, which contains large amounts of methane but very little of the unsaturated hydrocarbons, burn with an almost colorless, non-luminous flame. If such gases are used for illumination, a gas mantle must be employed. Before the extensive use of electricity for lighting, the Welsbach gas mantle was an important illuminating device. These mantles consist of the oxide of thorium (99 per cent) and the oxide of cerium (1 per cent). When this mantle is suspended about a flame, it becomes incandescent and emits a brilliant light, which is much superior to the ordinary luminous gas flame.

28. Miners' Safety Lamp

Many of the disastrous explosions in coal mines result from the ignition of mixtures of

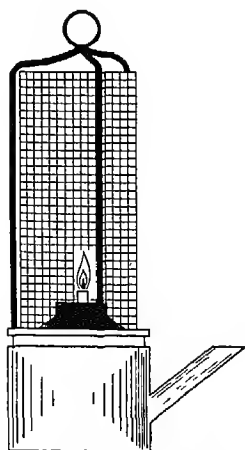


Figure 264 Miners' Safety Lamp

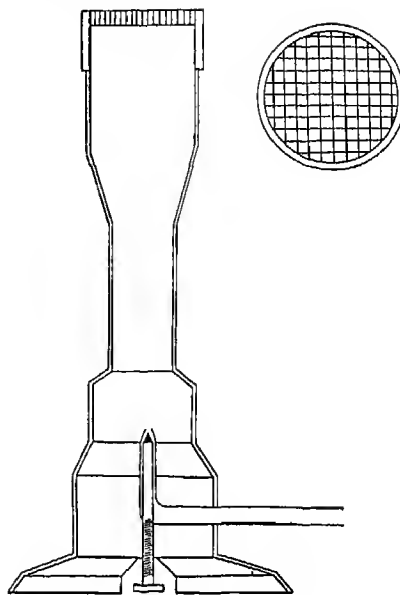


Figure 265 Meker Burner

air and coal dust or methane (fire damp). An open flame carried by a miner as a source of light is evidently very dangerous for this reason. In 1815, Sir Humphry Davy invented a safety lamp which can be carried by miners without much danger of igniting explosive mixtures. Davy's lamp (Figure 264) is based upon the principle that a flame may be extinguished if the temperature of the burning gases becomes less than their ignition point. The ordinary glass chimney is replaced by a wire gauze or screen. If a mixture of methane and air, for example, starts to burn near the flame and inside the gauze, it travels out to the screen, which conducts the heat away so rapidly that the mixture on the outside does not reach the ignition temperature. The principle of the safety lamp can be demonstrated by lowering a wire screen over a flame. The flame continues to burn beneath the screen, but the gases above are not heated to their ignition temperature. Or if a screen is placed above a burner, the gas above the screen may be ignited without affecting the gas below the screen. The Meker burner (Figure 265) makes use of the same principle. The

"striking back" of the flame is prevented by placing a screen at the top of the barrel of the burner. This screen prevents the gas in the barrel from becoming hot enough to ignite. The screen divides the flame into a number of small cones, and very rapid combustion is effected by admitting an excess of air at the base of the burner. A temperature some 400° higher than that obtainable with an ordinary Bunsen burner may be produced by the Meeker burner.

29 Coal Gas

When coal is heated in the absence of air, the gases which are evolved are combustible. In plants operated principally for the production of municipal gas supplies, bituminous coal is used, since this gives more volatile substances than anthracite coal. Coal gas is also a by-product of the modern coke ovens, which are operated primarily for the production of coke. A coal-gas plant consists of the iron retorts, in which the coal is heated (Figure 266), the hydraulic main, condensers, water and oil scrubbers, a sulfur remover, and the gas-holder. The gases that escape from the retorts bubble through the water seal in the hydraulic main. Here a considerable portion of the tar is collected. In the condenser, the rest of the tar is separated, and this flows into a tar-well. The gases then pass into the first of the scrubbers. This is a tower which is filled with

loose coke. Water is sprayed in at the top of the tower, and ammonia and some of the hydrogen sulfide dissolve in it. In another scrubbing tower, heavy oil is used to dissolve benzene and toluene. The hydrogen sulfide is then removed in the purifier, which contains quicklime or moist ferric oxide. The gas is then stored in the gas-holder, from which it is forced out into the city's mains.

The composition of coal gas varies considerably with the kind of coal that is heated in the retorts and with the temperature. One ton of soft coal produces, as primary products, about 1300 pounds of coke, 120 pounds of tar, and 12,000 cubic feet of gas. From the gas there may be recovered from 10-25 pounds of ammonium sulfate, 10 pounds of benzene, and about 3 pounds of toluene. The tar also gives many valuable products, such as phenol, naphthalene, anthracene, and pitch (see page 571). The coal gas finally collected in the gas-holders contains about 30-50 per cent of hydrogen (by volume), 20-35 per cent of methane, 10 per cent of carbon monoxide, smaller amounts of unsaturated hydrocarbons, such as ethylene and acetylene, and vapors of benzene and toluene. The percentage of hydrogen increases, when high temperatures are used in distilling the coal. The luminosity of the coal gas flame depends upon the percentage of unsaturated hydrocarbons in the mixture, since these are decomposed more readily into free carbon than the saturated hydrocarbons.

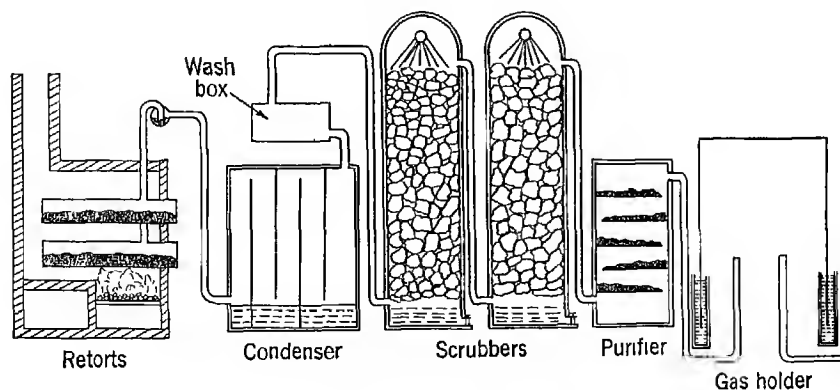


Figure 266 Coal Gas Plant

30 Water Gas

The production of water gas by passing steam through beds of red-hot coke has already been discussed (page 111). This gaseous mixture contains hydrogen and carbon monoxide. The flame of this gas is hot but non-luminous. Water gas is an excellent fuel but has no value for lighting purposes, unless the Welsbach mantle is used. It is often enriched by the addition of hydrocarbons from petroleum. The hot gas passes upward through a tower filled with brick over which oil is sprayed from the top of the tower. The vapors from the oil, mixed with water gas, then pass into another heating chamber where the hydrocarbon molecules are cracked. The changes that occur during cracking result in the formation of considerable quantities of unsaturated hydrocarbons, tar, and gas carbon. The tar must be removed by scrubbing. In addition to producing a gas that burns with a luminous flame, the enrichment of water gas in this manner adds substances that can be detected by their odors. This allows the detection of the gas with its poisonous carbon monoxide content, water gas that has not been enriched is odorless and therefore much more dangerous. The use of water gas as a source of hydrogen has been mentioned in a previous chapter (page 111).

31. Producer Gas

A cheap fuel that is used rather widely in the industries is produced by blowing air through thick beds of hot coal. The carbon dioxide that is produced in the lower portions of the coal is reduced to carbon monoxide at the higher levels. Some steam is blown in along with the air, and this is reduced to hydrogen by the reaction with hot coal. Not enough steam is used to cool the coal beds very much, and since the combustion of the coal (to form carbon dioxide) liberates a large amount of heat, the reaction goes on continuously. Gases, such as methane, are distilled from the coal. Hence, the principal constituents of producer gas are hydrogen,

carbon monoxide, methane and other hydrocarbons, carbon dioxide, and nitrogen. Producer gas is used as a fuel in gas-burning industrial furnaces and also, when mixed with air, in internal combustion engines. It is most often made in the same plant where it is used. If the gas is produced as required, it is possible to use it while still hot, thereby saving some energy and doing away with the necessity of supplying large gas-holders for storage.

32 Blast-Furnace Gas

Iron ores are reduced to metallic iron by heating the ores, which are usually oxides, with coke in the blast furnace. The heat is supplied by burning some of the coke in a blast of air that is blown into the furnace. The gases that escape contain carbon monoxide and some hydrogen, which comes from the reduction of the water that is present in the ores. The gas also contains nitrogen and carbon dioxide. In general, it resembles producer gas, but it is of a lower quality because of its greater percentage of non-combustible components.

NATURAL RUBBER

33 Chemical Nature of Rubber

The world's supply of rubber comes from a tree that grows wild in certain tropical regions, and which is also cultivated on "rubber" plantations. The trees are "tapped" by cutting through the bark, and from the cuts there flows a liquid, called *latex*, which is an emulsion of small rubber particles dispersed in water. The emulsion is stabilized by the presence of nitrogenous substances, which act as protective colloids. The addition of acetic acid precipitates these substances, and causes the separation of the rubber from the dispersing medium. The rubber that separates is in the form of a soft dough-like mass and is white if pure. To coagulate the latex from the wild trees, wooden paddles are dipped into it and then held in an acrid wood smoke. When the

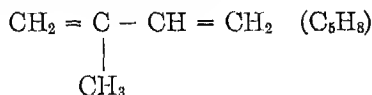


Courtesy of United States Rubber Company

Figure 267 Tapping a Rubber Tree

acid in the smoke has coagulated the rubber, the paddle is again dipped into the latex, and so on. This process results finally in the accumulation of a large ball of rubber on the end of the paddle.

The coagulated rubber, if pure, consists of a complex hydrocarbon, which is a polymerized form of *isoprene*.



The polymer (rubber) is sometimes called *caoutchouc* and, since its exact molecular structure is unknown, it is represented by the formula $(\text{C}_5\text{H}_8)_x$.

34 Properties and Uses of Rubber

Pure rubber becomes brittle in cold weather and in warm weather is entirely too soft and sticky to be of any use in the manufacture of rubber articles. These difficulties are prevented by *vulcanizing* the rubber. This process consists in heating the raw rubber with small amounts of sulfur or sulfur

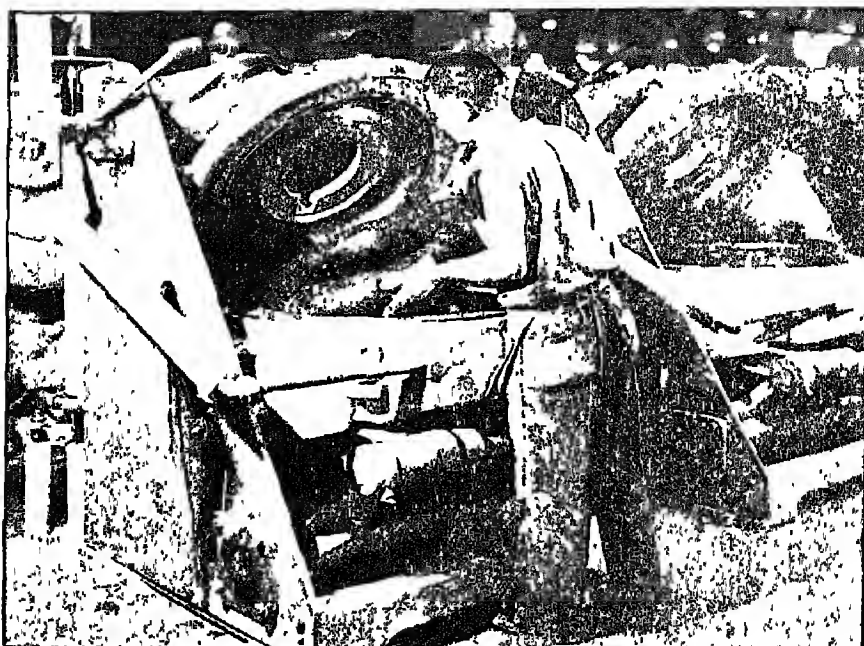
monochloride, S_2Cl_2 . The exact nature of the chemical change involved is not known. Some of the atoms of sulfur, however, must become attached by forming bonds with carbon atoms that are joined by double bonds in the rubber molecule. From 5 to 30 per cent of sulfur is added during vulcanization. Small amounts are used in making soft and elastic vulcanized rubber, while hard rubber, or *ebonite*, results when larger amounts of sulfur are added. Small percentages of certain organic compounds act, catalytically, to increase the speed of vulcanization. These substances are called *accelerators*.

Most rubber articles contain several substances in addition to rubber and sulfur. Red rubber contains antimony sulfide, and black rubber contains carbon black. Not only do these substances impart color to the finished product, but many of them increase the resiliency, strength, toughness, and resistance to wear. Zinc oxide is very often added to impart these qualities to the rubber used in the treads of automobile tires. Since 1927, the average mileage of tires has been more than doubled by the use of these substances, and also by improvement in the fabric used in the manufacture of tires.

The extent to which the automobile industry depends upon rubber is shown by the fact that the average car has 200 parts made of, or containing, rubber. About 145 pounds is used in the manufacture of each car. In addition, rubber is used in some 32,000 articles. Altogether, these uses consume about 1,100,000,000 pounds of rubber annually in the United States.

Review Exercises

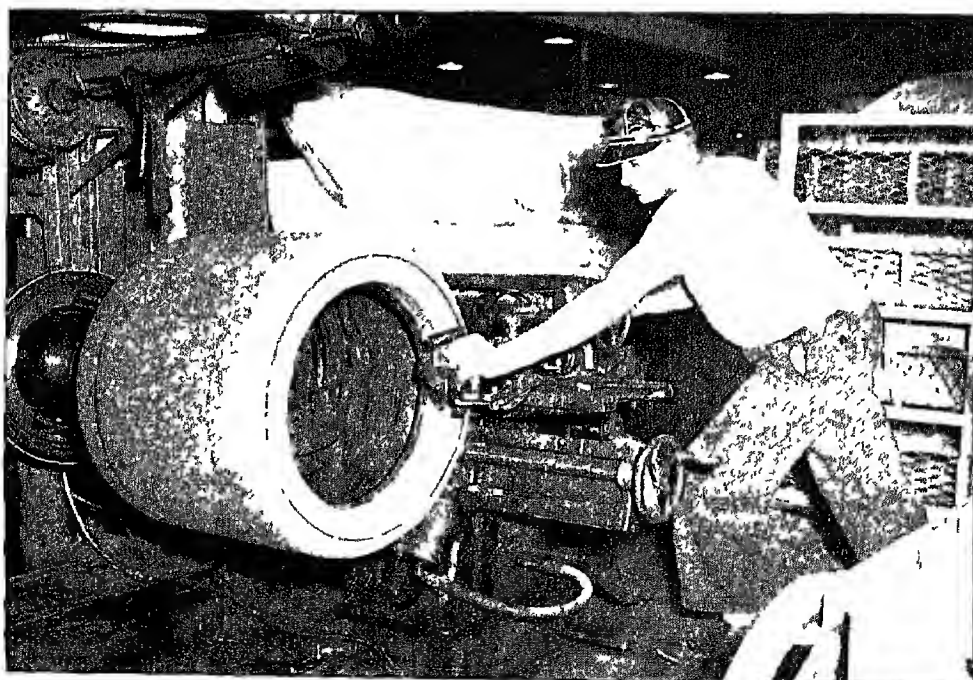
1. How is the large number of organic compounds explained?
2. What does the term *homologous series* mean as used in referring to hydrocarbons?
3. Give the name and structural formula of one member of each of the four series of hydrocarbons.
4. How are the unsaturated hydrocarbons dif-



Courtesy of The Goodyear Tire and Rubber Company

Figure 268 Vulcanizing Tubes for Tires

The rubber to make tubes is mixed with sulfur and other substances and then heated with steam under pressure



Courtesy of The Goodyear Tire and Rubber Company

Figure 269 Making Automobile Tires

- ferent in structure and in chemical properties from the saturated hydrocarbons? Give an example of each class of hydrocarbons
- 5 Define isomers. Illustrate by giving the structural formulas of the isomers that correspond to the empirical formula C_7H_{16}
 - 6 Suggest as many different isomers as you can for the empirical formula C_5H_{12}
 - 7 What are the differences in the composition of gasoline, kerosene, and lubricating oils?
 - 8 What does the term *cracking* mean as applied to the production of gasoline?
 - 9 How is ethylene produced from grain alcohol (C_2H_5OH)? How is the same alcohol made from ethylene?
 - 10 Calculate the densities of methane, ethylene, and acetylene (in their gaseous states and under standard conditions) from their formulas
 - 11 How many calories of heat are evolved during the combustion of 10 standard liters of methane?
 12. Why is a high pressure favorable to the reactions involved in the Bergius process of "liquefying coal"?
 - 13 From what source are benzene, toluene, and xylene obtained? How do the structures of these hydrocarbons differ?
 - 14 Why is a flame of burning hydrogen not luminous? Why do unsaturated hydrocarbons produce flames that are more luminous than those produced by saturated hydrocarbons?
 - 15 How and why is water gas enriched?
 - 16 Explain the principles upon which the Welsbach gas mantle and the miners' safety lamp are based
 - 17 Which of the following hydrocarbons will produce the greatest quantity of water when one gram-molecular weight of each is burned? Benzene, acetylene, ethane, and toluene
 - 18 Why are coal gas and water gas considered more valuable fuels than producer gas?
 - 19 A sample of gas containing ethylene and hydrogen was burned, forming 18 g of water and 22 g of carbon dioxide. What volume did the original gas sample occupy under standard conditions?
 - 20 If water gas can be represented as an equal molecular mixture of hydrogen and carbon monoxide, what volume of air (21 per cent oxygen) will be required to burn completely 10 liters? Assume standard conditions in calculating the volume of air
 - 21 The octane number of a gasoline is 90. Explain
 22. Identify isoprene, xylene, oil shale, polymerization, reducing flame, naphthalene, paraffin base oils, marsh gas, isobutane
 - 23 Complete the simple, or empirical, formula of one hydrocarbon containing eight carbon atoms (per molecule) in each of the four series of hydrocarbons
 - 24 Would you expect to obtain one, two, or more different compounds when chlorine reacts to replace one atom of hydrogen in the molecule of normal butane? Explain
 - 25 Explain the nature of the changes involved in each of the following processes used in the gasoline industry: alkylation, reforming, polymerization, hydrogenation
 - 26 Two gram-molecular weights of methane contain the same weight of carbon and four times as much hydrogen as one gram-molecular weight of acetylene. More heat is liberated, however, by the combustion of the latter. Explain
 - 27 "High test" gasoline contains hydrocarbons of smaller molecular weight than "low test" gasoline. For equal volumes of the vapors of the two grades of gasoline, at the same temperature and pressure, which liberates during combustion the greater quantity of energy? Explain

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DERIVATIVES OF THE HYDROCARBONS

*I turned my chair to the fire and dozed Again the
atoms were gamboling before my eyes Long
rows turning and twisting in snake-like motion
But look! What was that? One of the snakes had
seized hold of its own tail, and the form whirled
mockingly before my eyes As if by a flash of
lightning I awoke*

KEKULE

1 Alkyl Radicals

Many organic compounds are produced by the substitution of various kinds of atoms and radicals for one or more of the hydrogen atoms of a hydrocarbon molecule. Substances of this kind are called *derivatives* of the hydrocarbons. Some of them occur in different plant and animal products, and these can be changed by means of certain chemical reactions into other derivatives. On the other hand, some of the derivatives are, or may be, produced directly or indirectly from the hydrocarbons themselves by the method of substitution. The group remaining after the replacement of one hydrogen atom in the molecule of a methane hydrocarbon is called an *alkyl* radical. The alkyl radicals corresponding to the first ten members of the methane series of hydrocarbons are

Methyl CH_3	Hexyl C_6H_{13}
Ethyl C_2H_5	Heptyl C_7H_{15}
Propyl C_3H_7	Octyl C_8H_{17}
Butyl C_4H_9	Nonyl C_9H_{19}
Amyl C_5H_{11}	Decyl $\text{C}_{10}\text{H}_{21}$

For the most part, we shall confine our discussion to the derivatives of the methane series of hydrocarbons, but in the latter part of this chapter we shall also present some of

the derivatives of benzene, toluene, and other aromatic hydrocarbons. Speaking, for the present, of the derivatives of methane and its homologues, and of the compounds which contain only oxygen in addition to carbon and hydrogen, we find that six classes of derivatives make a convenient grouping of many organic compounds of great importance. These six classes are discussed below.

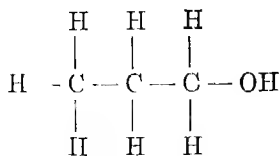
2 The Alcohols

Derivatives of hydrocarbons that contain one or more hydroxyl groups in place of one or more hydrogen atoms of the molecule are called *alcohols*. The most familiar alcohols are those which contain the methyl and ethyl alkyl groups, and which may be regarded as derivatives of methane and ethane, respectively.

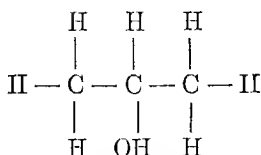
Methyl alcohol CH_3OH
Ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$ or $\text{C}_2\text{H}_5\text{CH}_2\text{OH}$

For each of the first two alcohols only one structural formula is possible, and there are, therefore, no isomers of these substances. Isomerism makes its appearance in propyl alcohol, which has two isomeric forms. Four isomers of butyl alcohol exist, and the number of possible isomers corresponding to the

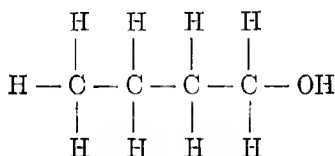
empirical formula $C_{13}H_{27}OH$ reaches into the hundreds



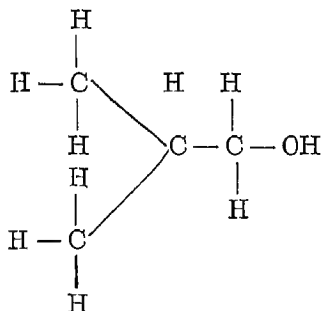
Normal (n) propyl alcohol



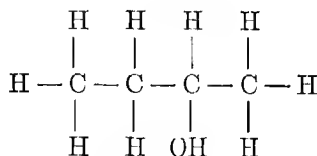
Isopropyl or secondary propyl alcohol



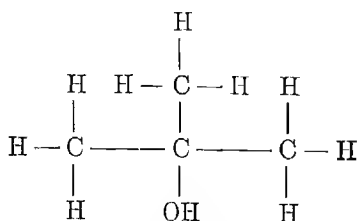
Normal butyl alcohol



Isobutyl alcohol



Secondary butyl alcohol



Tertiary butyl alcohol

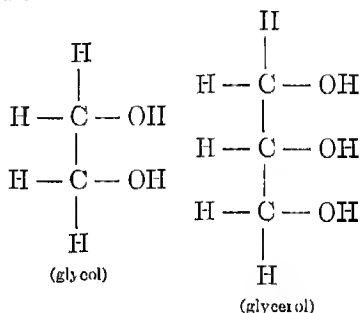
The names methanol, ethanol, propanol, and so on, are sometimes used to designate the different alcohols, the ending *-ol* indicating the presence of the hydroxyl group. The terms *primary*, *secondary*, and *tertiary* alcohols, as used above, refer to compounds in which the following groups appear

Primary — CH_2OH

Secondary — $CHOH$

Tertiary — COH

All of the substances named above are *monohydric* alcohols. *Glycol* and *glycerine* (glycerol) are dihydric and trihydric alcohols, respectively. The former contains two and the latter contains three hydroxyl groups per molecule.



There are several glycols. The substance represented by the formula $C_2H_4(OH)_2$ is ethylene glycol, which is used as an anti-freeze in automobile radiators. For this purpose it is preferable to methyl and ethyl alcohols because of its relatively high boiling point, 197.4° .

3 Glycerine

Glycerine, or *glycerol*, is a by-product of the soap industry. Fats are compounds derived from glycerine and certain organic acids, when a fat is treated with sodium hydroxide, the acid is converted into soap — a sodium salt of the acid — and glycerine is set free. Glycerine can also be produced by synthetic processes, and it is produced in small amounts during the fermentation of sugar to make ethyl alcohol. Even during World War I, this method — sugar fermentation — was used extensively in Germany,

and it is said that the percentage of glycerine in the solution resulting from the fermentation could be increased to an amount corresponding to about one third of the sugar consumed in the reaction. The production of glycerine by this and by other methods for use in making nitroglycerine becomes important when fats must be conserved for use as food.

Glycerine is a colorless, oily, sweet-tasting liquid. Besides its rôle in the manufacture of nitroglycerine, it is used to prevent the drying-out of many products, such as ink, cigarettes, and smoking-tobacco, and as an antifreeze in automobile radiators. It is miscible with water in all proportions, and pure glycerine is very hygroscopic. This property makes glycerine suitable for use in lotions, soaps, and cosmetics. Because of its sweet taste it is also used in medicines and confections.

4 Methyl Alcohol (Methanol) CH_3OH

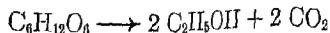
Until about 1925, this alcohol was produced almost universally by the destructive distillation of wood (page 292). For this reason it came to be known as *wood alcohol*. Hard woods, such as birch and beech, are used. The yield is about two gallons of alcohol per ton of wood. At the present time, methanol is produced catalytically by the direct combination of hydrogen and carbon monoxide. A somewhat modified water-gas mixture is heated under pressure and in the presence of zinc oxide, or other catalysts, to bring about the reaction. When this process was first put into operation in Germany, methanol could presumably be manufactured in that country and shipped to the United States at a price considerably lower than the price of the methanol produced in this country by the wood distillation industries. Industrial plants using the synthetic process are now operated in the United States, and in many other parts of the world. In one modification of the process, carbon dioxide is used instead of carbon monoxide. Methanol is a colorless liquid, which boils

at about 66° . It is extremely poisonous when taken internally, or when the vapor is breathed. It produces blindness, by its action on the optic nerve, and often causes death. Industrially, methanol is a very important liquid and chemical reagent. It is widely used as an antifreeze and as a solvent in the manufacture of certain substances, such as varnishes and shellacs. It is also used extensively in the manufacture of formaldehyde, dyes, and drugs, and as a denaturant of ethyl (grain) alcohol.

5 Ethyl Alcohol (Ethanol) $\text{C}_2\text{H}_5\text{OH}$

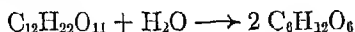
We have mentioned, in the preceding chapter, the production of ethyl alcohol from ethylene. This process is now used commercially on a large scale. The production of ethyl alcohol in wine, beer, and other alcoholic beverages, as well as a large part of the supply of industrial alcohol, depends upon the fermentation of sugar or starch, a chemical change brought about by the action of certain substances produced by yeast. This process of producing alcohol should be called *alcoholic fermentation* to distinguish it from other changes in which microscopic organisms convert one substance into another. The souring of milk and the production of vinegar from cider, for example, are referred to as acid fermentations.

The reaction in which glucose is converted into ethyl alcohol also produces carbon dioxide



The starting material may be glucose itself, or other substances which can be converted readily into glucose or sugars similar to it. These substances include other sugars, such as sucrose (cane sugar) and maltose, fruit juices, which contain sugars, and starch, $\text{C}_6\text{H}_{10}\text{O}_5$. Even cellulose, which constitutes the woody structure of all plants, may be changed first into glucose and then into ethyl alcohol. Alcoholic fermentation is catalyzed by certain substances called

enzymes, which are produced by the yeast cells. The reactions in which enzymes are involved will be discussed at greater length in Chapter 38, where sugars, starch, and cellulose are presented. Ordinary cane sugar, starch, and cellulose are not changed directly into alcohol by yeast. Cane sugar, $C_{12}H_{22}O_{11}$, is first converted into simpler sugars that have the formula $C_6H_{12}O_6$ by an enzyme called *invertase* produced by the yeast cells.



These simpler sugars are then converted into alcohol by a second yeast-enzyme, called *zymase*. Starch must first be changed into sugars by boiling it with dilute hydrochloric acid solution or by the action of enzymes. Cellulose is also converted into sugar by boiling it with concentrated acid, and the sugar is then fermented by the action of yeast. However, cellulose is not the source of much glucose or alcohol at present.

Solutions containing 14 to 18 per cent of alcohol can be made directly by fermentation. At higher alcoholic concentrations the yeast cells are killed. Higher proportions of alcohol are obtained by the fractional distillation of the naturally fermented product. By this means, a solution containing 95–96 per cent of alcohol can be produced. Practically *absolute* (or approximately 100 per cent alcohol) can be produced by treating 95 per cent alcohol with some dehydrating agent, such as quicklime, and distilling. Absolute alcohol is usually prepared on an industrial scale, however, by adding benzene to 95 per cent alcohol and distilling this mixture. The first portion of the distillate, which contains the benzene, water, and some alcohol, is discarded.

Pure ethyl alcohol is a colorless liquid, which boils at 78.3° , has a density of 0.789 (20°), and freezes at about -117° . Next to water, it is the most widely used solvent. It is used in the extraction of certain organic compounds from natural materials and in the preparation of varnish, shellac, films,

lotions, dyes, medicines, flavoring extracts, tooth pastes, and hundreds of other industrial and pharmaceutical products. It is used in reactions leading to the production of ethylene, chloroform, ether, iodoform, and several thousand medicines. It may also be used as a fuel. Solid alcohol or "canned heat" is usually made from soap and alcohol. The use of alcohol as an antifreeze in automobile radiators is well known to everyone. During World War II, about 600,000,000 gallons of ethyl alcohol were produced annually in the United States.

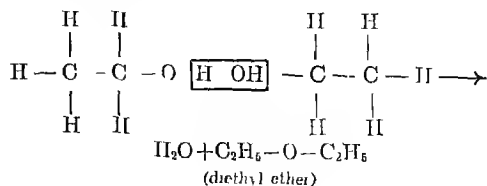
Wood alcohol is the most familiar denaturant of ethyl alcohol. Other denaturants are pyridine, low-boiling petroleum hydrocarbons, and *alcohol*, a product obtained by oxidizing kerosene. Denatured alcohol is sold without the payment of the tax imposed upon untreated ethyl alcohol.

Fusel oil is a mixture of alcohols — chiefly isomers of butyl and amyl alcohols — produced along with ethyl alcohol during fermentation.

6 The Ethers

The alcohols are dehydrated by the action of limited quantities of sulfuric acid at a temperature of about 150° to form substances called *ethers*.

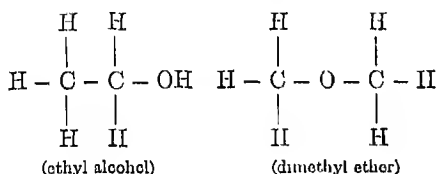
When ethyl alcohol is treated with a relatively small quantity of acid, *diethyl ether* is formed. The reaction which occurs may be represented by the following simplified equation, although intermediate steps which are not shown may occur.



Diethyl ether is the substance commonly called *ether*. It boils at 35° , and its vapor is highly inflammable. Its best known use is as an anesthetic for general surgery. It is an excellent solvent for some water-insoluble

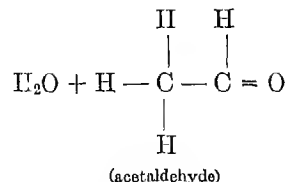
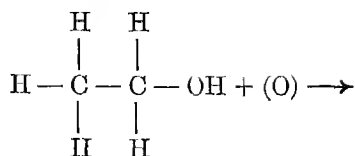
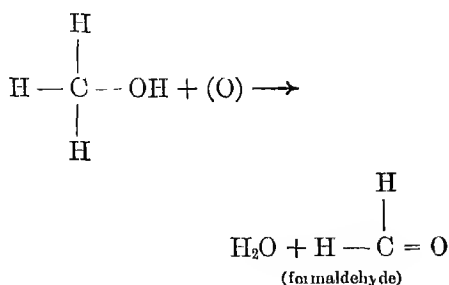
substances such as fats, waxes, and gums. It is used as a solvent for the extraction of fats in analytical chemistry, when products are analyzed for fat content. It is also used as a solvent in the manufacture of smokeless powder, collodion, and certain kinds of artificial silk.

The ethers correspond to the oxides of inorganic chemistry. The formula and nature of an ether varies with the alkyl radicals combined with oxygen. *Dimethyl ether* is $\text{CH}_3 - \text{O} - \text{CH}_3$, *Ethyl methyl ether* is $\text{C}_2\text{H}_5 - \text{O} - \text{CH}_3$, and *propyl ethyl ether* is $\text{C}_3\text{H}_7 - \text{O} - \text{C}_2\text{H}_5$. Dimethyl ether contains the same number of carbon, hydrogen, and oxygen atoms as ethyl alcohol, and the two substances have the same empirical formula, $\text{C}_2\text{H}_6\text{O}$. One substance is the isomer of the other.



7 Aldehydes

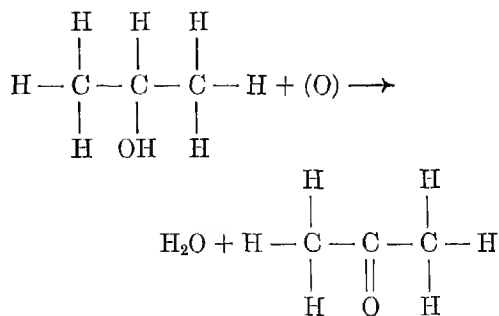
When the alcohols undergo combustion, they are oxidized to carbon dioxide and water. But if the oxidation is carried out, at a relatively low temperature, by some moderately active oxidizing agent, a substance called an *aldehyde* is produced, if the alcohol belongs to the class which we call *primary* alcohols. The general formula for an aldehyde is $\text{R} - \text{CHO}$, where R represents an atom of hydrogen or, more often, an alkyl radical. The production of the aldehydes corresponding to methyl and ethyl alcohols is shown by the following reactions:



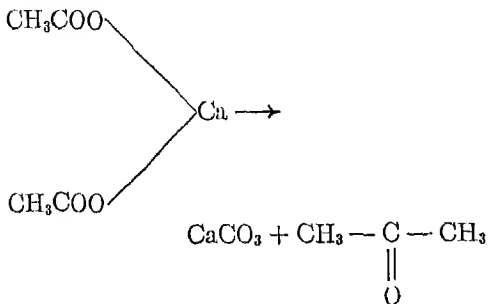
Formaldehyde is the most important of the aldehydes. It is produced whenever methyl alcohol is moderately oxidized. Its most important commercial use is in the manufacture of certain *plastics*, such as *Bakelite*. It is commonly known and used in the form of a 40 per cent solution, which is called *formalin*. This solution is used as a disinfectant and as a preservative of laboratory and museum specimens of organic material. Its use as a preservative of food is illegal because of its poisonous effects. It is used in disinfecting rooms which have been inhabited by persons with contagious diseases, and is also used as a disinfectant for grains and potatoes, and as a fly poison.

8 Ketones

The ketones are compounds that have the general formula $\begin{array}{c} \text{R} \\ | \\ \text{R} - \text{C} = \text{O} \end{array}$, where R represents an alkyl group; the two alkyl groups may be the same or different. Ketones can be produced by the oxidation of a *secondary* alcohol. Thus, *dimethyl ketone* is produced by the oxidation of secondary or isopropyl alcohol.



This substance is the most important of the ketones and is called *acetone*. It is one of the four important products (charcoal, methyl alcohol, acetic acid, and acetone) of the wood distillation industry (page 292). It may be prepared by heating dry calcium acetate.

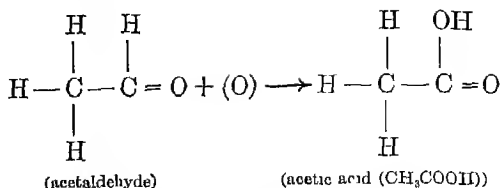
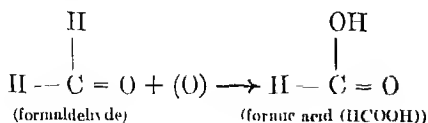


Acetone is also produced by certain fermentation-reactions and by a process in which ethyl alcohol and water react to form acetone, carbon dioxide, and hydrogen. The carbon dioxide and hydrogen produced in this reaction are used to make methyl alcohol.

Acetone is one of the most important organic solvents. As such it is used in the manufacture of varnishes, smokeless powders, paint and varnish removers, and many other materials. Its use as a solvent for acetylene has been mentioned previously (page 570).

9 Acids

Upon further treatment with moderately vigorous oxidizing agents, aldehydes are converted into compounds that have the properties of relatively weak acids. These acids contain the *carboxyl* radical —COOH . The hydrogen atom of the carboxyl group may be liberated as hydrogen ion. The following equations show the oxidation of formaldehyde and acetaldehyde to formic acid and acetic acid, respectively.



These two acids are the first members of a series commonly called the *fatty acids*, because some of them are found, combined with glycerine, in fats.

10. Formic Acid

This fairly strong acid is present in certain kinds of nettles and is responsible in part for the sting of these plants. It was produced, originally, by the distillation of a variety of ants. The sharp irritation and sting resulting from bites of ants and bee stings are the effect of formic acid. The acid is now made by heating carbon monoxide and sodium hydroxide under pressure and treating the product of this reaction with hydrochloric acid. Sodium formate, $\text{H} - \text{COONa}$, is first produced; this salt then reacts with HCl to release formic acid, $\text{H} - \text{COOH}$.

11. Acetic Acid

This well-known acid is produced from ethylene (page 570), from the products of the distillation of wood, or by the conversion of ethyl alcohol in dilute solution into the acid under the influence of certain bacteria. The pyroigneous distillate (page 292) produced when wood is heated in the absence of air is treated with lime, which converts acetic acid into calcium acetate. After the solution has been evaporated to dryness, this salt is treated with sulfuric acid, and the mixture is distilled. Acetic acid is volatile and, consequently, is easily recovered.

The production of acetic acid from ethyl alcohol involves the reactions that occur when cider is allowed to stand exposed to the air for some time. The sugars of the fruit juice are first fermented to produce ethyl alcohol. The "hard cider" is then placed in a container that has previously contained vinegar, or "mother of vinegar" is added, in order that the proper bacteria may be ob-

tained to complete the oxidation of alcohol to acetic acid. The reaction is slow, but it can be accelerated by circulating the solution containing the alcohol through a mixture of beechwood shavings and "mother," which contains the acetic acid-forming bacteria. The shavings give a greater amount of surface. Cider vinegar contains 4 to 5 per cent of acetic acid and has a brown color. "White" or "wine" vinegar is made by the action of bacteria upon colorless alcoholic solutions, or by simply mixing pure acetic acid and water.

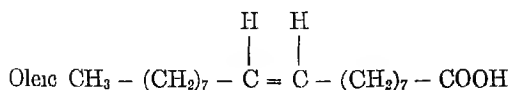
The anhydrous, pure acid is called *glacial* acetic acid, because of the ice-like solid that it forms when cooled to 16.7° .

Acetic acid has many uses. It is used to prepare calcium acetate, from which acetone is derived, to make lead acetate, which is known as "sugar" of lead, in the manufacture of many dyes and other coal-tar products, such as aspirin, to produce cellulose acetate, which is somewhat similar to cellulose nitrate (page 485), to react with various alcohols in manufacturing compounds valuable as solvents and artificial flavors, in dyeing, and in the printing of silk and wool cloth. Cellulose acetate has the advantage over pyroxylin (cellulose nitrate) of non-inflammability. The product of the reaction of acetic acid with amyl alcohol is amyl acetate, or banana oil, which is a solvent extensively used in the production of pyroxylin lacquers, bronzing liquids, and so forth.

12 Other Organic Acids

The formulas and names of other more or less common *monobasic* organic acids are listed below.

Propionic	$\text{CH}_3 - \text{CH}_2 - \text{COOH}$
Butyric	$\text{CH}_3 - (\text{CH}_2)_2 - \text{COOH}$
Valeric	$\text{CH}_3 - (\text{CH}_2)_3 - \text{COOH}$
Caproic	$\text{CH}_3 - (\text{CH}_2)_4 - \text{COOH}$
Palmitic	$\text{CH}_3 - (\text{CH}_2)_{11} - \text{COOH}$
Stearic	$\text{CH}_3 - (\text{CH}_2)_{18} - \text{COOH}$



Oleic acid is unsaturated. The other acids in this list correspond to members of the methane series of hydrocarbons.

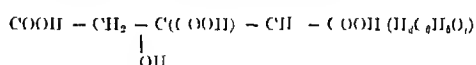
Lactic acid, which is produced when milk sours, has the formula $\text{CH}_3\text{CHOH} - \text{COOH}$. As its formula indicates, this acid is also an alcohol. Its presence in sour milk results from the action of certain bacteria upon milk sugar. The formation of this acid is responsible for the destruction of the colloidal condition of the casein of milk and its precipitation as curds.

Oxalic acid is dibasic, that is, the molecule contains two carboxyl groups, each of which may liberate a hydrogen ion. Its formula is



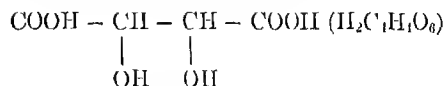
A moderately strong acid, it is found, usually as the acid potassium salt, in sorrel, rhubarb, and certain plants that have a sour taste. The oxalate ion, $\text{C}_2\text{O}_4^{--}$, is used in the detection of calcium in analytical chemistry, since calcium oxalate is only very slightly soluble in water. The acid itself is used in cleaning and polishing door plates, brass rails, and other metallic articles, in cleaning straw hats, in making ink-removers, in dyeing and printing cotton cloth, and in bleaching straw and leather. The acid is poisonous.

Citric acid. This is a tribasic acid.



It is present in citrus fruits — lemons, grapefruits, oranges, and limes. Magnesium citrate is used in medicine, and the acid itself is widely used in the manufacture of beverages.

Tartaric acid is a dibasic acid.

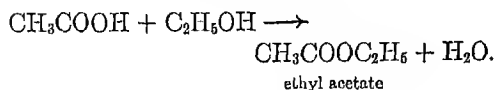
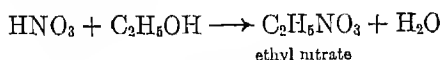


Crude tartar, from which the acid is prepared, collects in the containers in which wine or grape juice is stored. Three salts of this acid are important substances. These are *cream of tartar*, $\text{KHC}_4\text{H}_4\text{O}_6$ (page 384), *Rochelle salts*, $\text{KNaC}_4\text{H}_4\text{O}_6$, and *potassium antimonyl tartarate* (tartar emetic), $\text{KSbOC}_4\text{H}_4\text{O}_6$ (page 525).

13. Esters

Esters are the products of the reactions of

acids with alcohols. These reactions are somewhat like the neutralization of acids by bases, but the alcohols differ from the hydroxide-bases; they are not electrolytes and produce no hydroxyl ions. The esters are analogous to inorganic salts, but differ from salts in that they are not electrolytes. Because the alcohols are not ionized, the reactions by which esters are formed proceed very slowly at ordinary temperatures. Esters may be produced from both organic and inorganic acids.



Since glycerine is an alcohol, it may also form esters. Nitroglycerine (page 485) is the glyceryl ester of nitric acid. Similarly, cellulose acetate and cellulose nitrate are esters of cellulose, which acts as an alcohol in their formation, and acetic and nitric acids.

Many of the esters have pleasant, flower-like or fruit-like odors. They are used in perfumes, as solvents, and as flavors. Amyl acetate is "banana oil," and ethyl butyrate possesses the flavor of the pineapple.

14. Fats

The fats are esters of glycerine and certain monobasic organic acids. The most familiar fats are glyceryl esters of palmitic, stearic, and oleic acids (page 587). These esters are called *palmitin*, *stearin*, and *olein*, respectively.

Palmitin $(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_3\text{C}_3\text{H}_5$

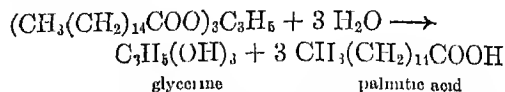
Stearin $(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_3\text{C}_3\text{H}_5$

Olein $(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_3\text{C}_3\text{H}_5$

These three esters have widely different melting points, therefore, the hardness of a fat depends upon the relative amounts of the three esters that it contains. The liquid fats, such as olive oil, coconut oil, and cottonseed oil, contain 75 per cent or more of the ester of oleic acid, which is a liquid. Beef

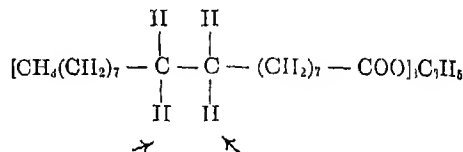
tallow, on the other hand, contains about 25 per cent of olein and 75 per cent of palmitin and stearin. It is one of the hardest of the natural fats. Lard, which is a softer and more readily melted fat, contains 50 to 60 per cent of olein and about 40 per cent of palmitin. Butter, in addition to 12 to 14 per cent of water, contains olein and palmitin and about 8 per cent of butyrim, the glyceryl ester of butyric acid $(\text{CH}_3(\text{CH}_2)_2\text{COOH})$.

Rancidity of fats results when the esters are hydrolyzed.

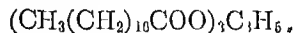


The foul odor of rancid butter is caused by the free butyric acid, which is liberated when the fat hydrolyzes.

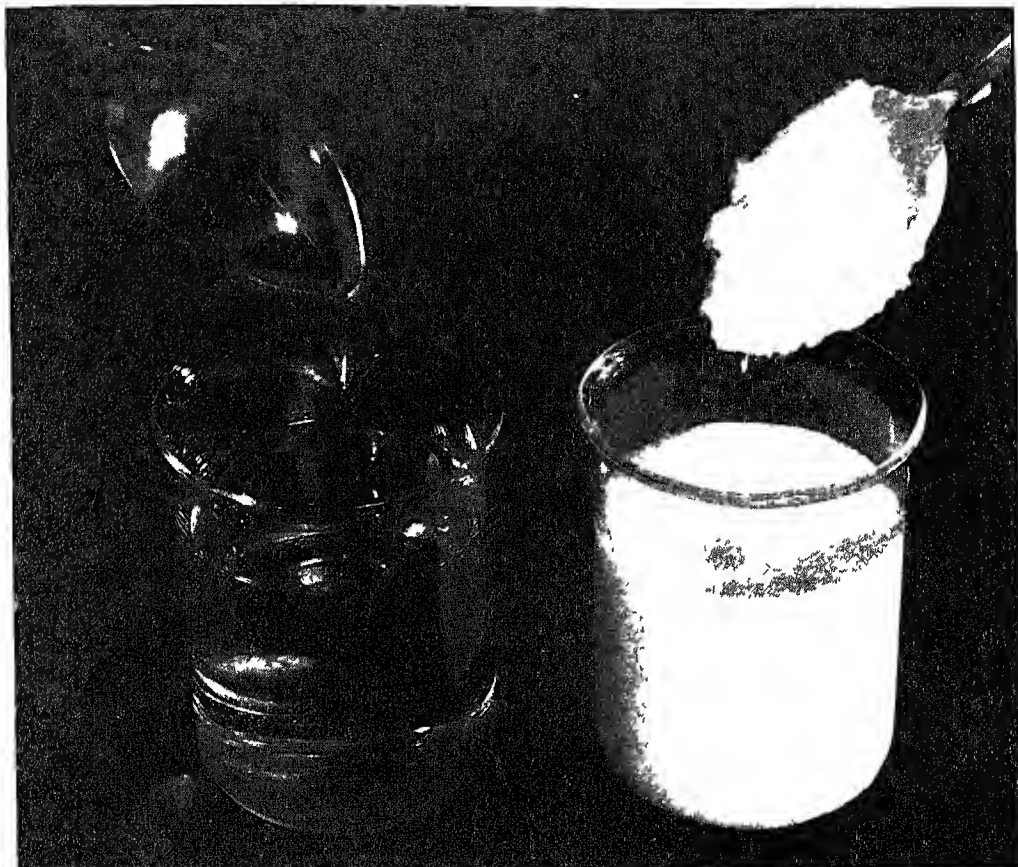
The hydrogenation of a liquid fat (page 114) involves the addition of hydrogen, which combines with the carbon atoms that are linked together by the double bond in the molecule of olein.



This reaction converts olein into stearin, which is a solid fat.



This is the method used in producing solid fats from cottonseed oil, coconut oil, and other vegetable and some animal oils. The solid fats thus produced are used in the manufacture of soap, as shortening, and as oleomargarine. Some kinds of oleomargarine are produced by mixing stearin from beef fat with oils to give a fat of about the same consistency and melting point as butter. The yellow color of butter is obtained by adding a yellow dye, which is usually enclosed with the package of oleomargarine in a small envelope and is mixed by the consumer. High taxes are imposed upon oleomargarines that are colored before they are



Courtesy of Proctor and Gamble

Figure 270 Effect of Hydrogenation

The oil on the left is liquid and runs off the spoon. The material on the right has been hardened by hydrogenation and, therefore, is no longer liquid at room temperature.

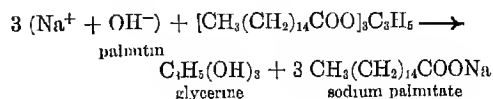
sold. The idea appears to be that the customer must know that he is buying a substitute for butter. Hydrogenated fats and those prepared by mixing solid and liquid esters to give a product of the correct degree of hardness are as clean and nutritious, when used as foods, as the natural products. They should melt, however, at the body's temperature. The flavor of butter is sometimes added to the substitutes by churning the fats with milk or buttermilk.

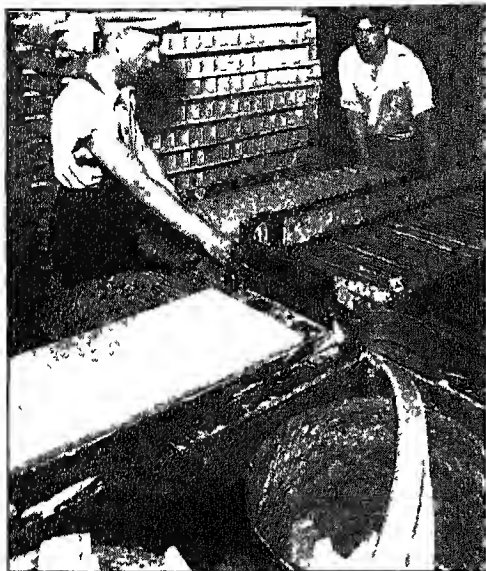
15 Soaps and Saponification

Soaps are salts (usually sodium or potassium salts) of certain "fatty acids." Most soaps are made by treating fats with an

alkali, such as sodium hydroxide, but some are produced by treating the free fatty acids with alkali. The free acid is made by hydrolyzing a fat (page 588) with the aid of dilute sulfuric acid which acts as a catalyst.

Fats are esters of glycerine and the fatty acids. These esters react with an alkali, such as sodium hydroxide, to form glycerine and a salt of the acid. For example, sodium hydroxide reacts with glyceryl palmitate, the ester of glycerine and palmitic acid, to form glycerine and sodium palmitate, a soap.





Courtesy of Philadelphia Quartz Company

Figure 271 Cutting Laundry Soap into Bars

This reaction, and similar reactions between the various glyceryl esters (fats) and sodium or potassium hydroxides, are called *saponification*.

The ordinary "hard" soaps are made by using sodium hydroxide and the harder fats, that is, those containing high proportions of stearin and palmitin. The "soft" and liquid soaps are made from potassium hydroxide and liquid fats containing a high percentage of olein.

Naturally, the cheaper fats which are not desirable as foods are used in soap-making. These are boiled in the "soap kettle" with sodium hydroxide, and the soap is produced in a colloidal state from which it is precipitated or "salted out" by the addition of sodium chloride. The soap settles out on the top of the mixture in the kettle. It is removed and washed, first, with a salt solution, and then with water. It next goes to the "cutcher" where it is mixed with various substances such as coloring materials, perfumes, and fillers. The fillers, which may be borax, sodium silicate, sodium carbonate, and rosin, are usually added only to the cheaper grades or to laundry soaps. These fillers usually serve some purpose. Borax, sodium silicate, and washing soda (sodium carbonate) give alkaline solutions

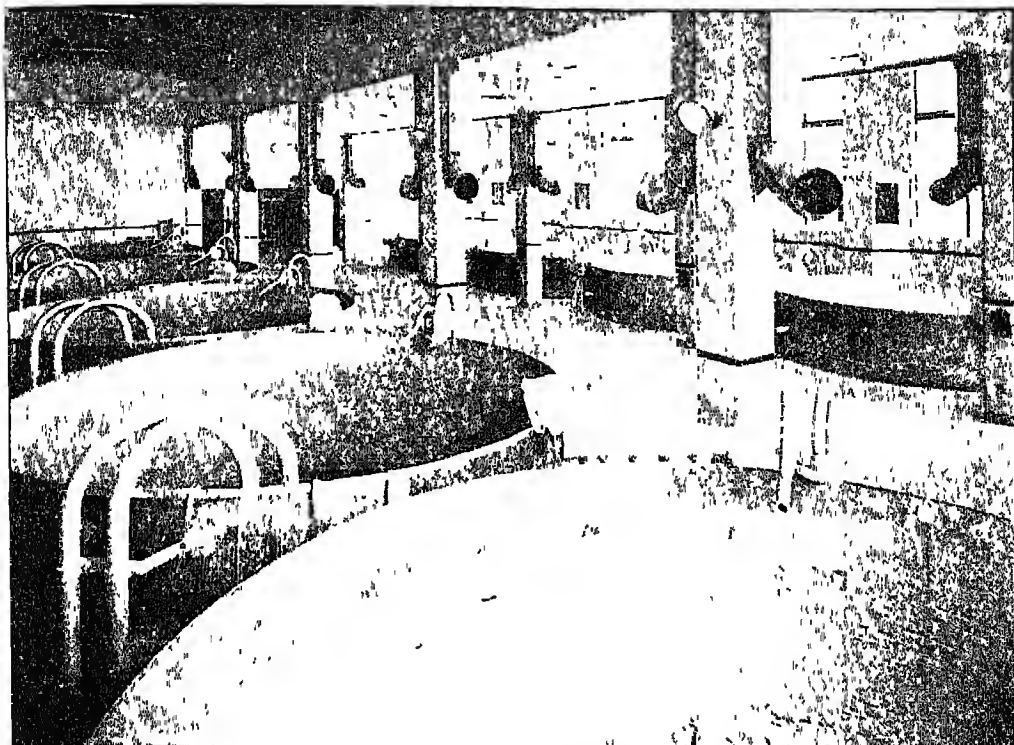
in water and aid in softening water, while rosin increases the lathering qualities of the soap. From the "cutcher," or mixer, the soap is run into molds or "frames." The hardened soap is then cut into cakes. Toilet soaps are usually prepared from fats that are liquid or semi-liquid at ordinary temperatures. Laundry soaps are made from hard fats. Floating soaps contain air bubbles, which are incorporated with the soap in the "cutcher." Transparent soaps are made by adding sugar or glycerine, or they are made by dissolving dry soap in alcohol and evaporating the excess of solvent. Upon standing the soaps lose all the alcohol with which they are mixed and become transparent. A good toilet soap should be practically pure sodium oleate, stearate, or palmitate and should contain little or no free alkali. Different soaps may contain different perfumes and colors, but the value of a soap as a cleansing agent does not depend upon these ingredients. Many of the substances added to soaps do serve useful purposes, however. Scouring soaps contain large percentages of abrasive materials, such as diatomaceous earth, clay, finely powdered silica, or volcanic ash. Soap powders may contain only about 10 to 25 per cent of soap. The remainder is frequently sodium phosphate and sodium carbonate.

After the removal of the soap from the kettle in which the saponification is carried out, the solution is concentrated by evaporation, and the glycerine is recovered by distillation.

16 The Properties and Cleansing Action of Soaps

In using a soap one desires to remove grease and particles of dirt. It was formerly thought that the cleansing action of a soap depends upon the free sodium or potassium hydroxide that is liberated by hydrolysis when the soap is added to water; the quantity of alkali produced by the hydrolysis of a soap is now known, however, to be too small to have much effect.

The soap itself is responsible for the cleansing action, which depends upon several factors. The most important of these is the ability of the soap to act as an emulsifying agent in the formation of an emulsion of oil and grease in water. In this way, the grease on skin or cloth is broken up into small drop-



Courtesy of Lever Brothers

Figure 272 Kettle House
Showing the empty soap kettles where the fats are boiled.

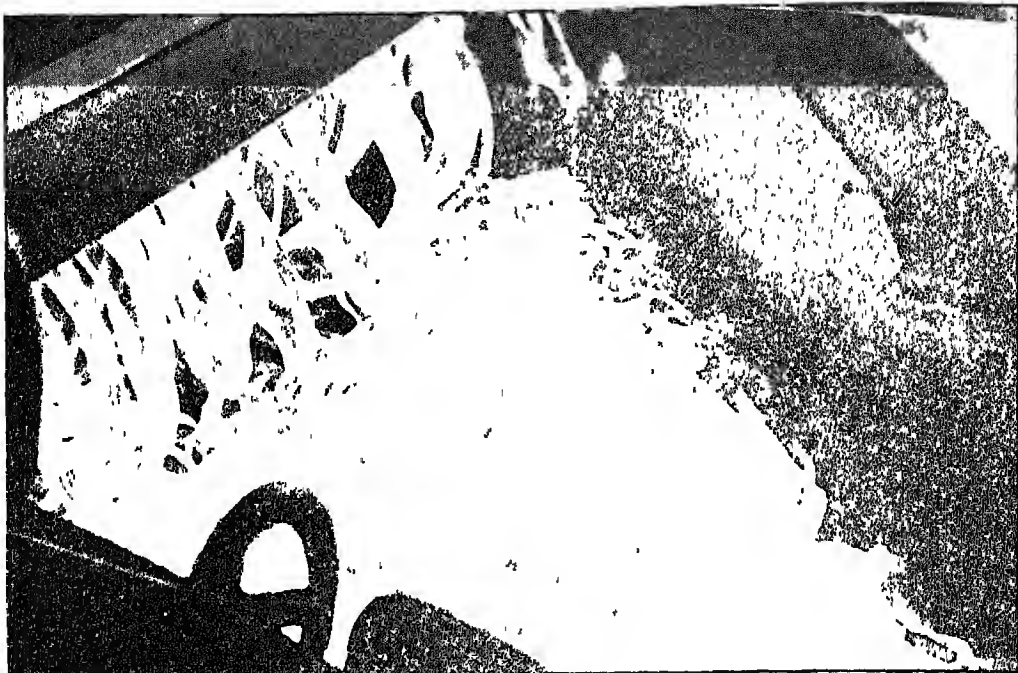
lets, which are prevented from coalescing by the soap that surrounds each droplet and acts as a protective colloid. These droplets are then washed away in an excess of water.

As an explanation of the action of soap in stabilizing an emulsion of droplets of oil in water, it has been suggested that the soap molecules — consisting as they do of long chains of atoms — dissolve at one end in oil and at the other end in water. The end of the molecule consisting of $-\text{COONa}$, like other sodium salts, is more soluble in water than in oil, while the other end of the molecule, consisting of a hydrocarbon radical, is more soluble in oil as all hydrocarbons are. The soap molecules, therefore, form a boundary between oil and water (Figure 274), and act to bind the two liquids together. Since there is usually much water and only a small amount of oil, there must be a very large oil-surface in which the hydrocarbon ends of all the soap molecules can dissolve. This extensive surface is produced only when the oil is broken up into many small drops, because the extent of

the surface increases as matter is divided into smaller and smaller particles (page 555). These small drops of oil can be dispersed in water for some time without coalescing to form a layer of oil.

The cleansing action of soap also depends upon the effect of soap upon the surface tension of water. Soap solutions have a lower surface tension than pure water. This property causes water containing a soap suspension to spread very readily over surfaces and to penetrate the pores of the skin or the spaces between the threads of cloth. The removal of particles of dirt depends, at least in part, upon the ability of the colloidal soap material to adsorb and carry away the dirt.

A mixture of soap and water is a colloidal dispersion instead of a true solution. If calcium and magnesium ions are present in the water, then salts of palmitic, stearic, and oleic acids are not soluble, and they do not form colloidal dispersions. For this reason, the addition of soap to hard water produces a



Courtesy of The Procter and Gamble Company

Figure 273. Cutting Soap into Ribbons in the Manufacture of Soap Flakes

curdy precipitate of calcium and magnesium soaps, and hence the soap does not form a lather, or "suds." Enough soap must be added to precipitate the calcium and magnesium ions of the hard water as "insoluble" soaps, before the soap can have any cleansing action. This results in a waste of soap and is also undesirable in the laundry, because the insoluble soaps are left upon the cloth as gray, dirty deposits. Some soaps made for use in hard waters contain a water softener, such as sodium carbonate, which dissolves and reacts to precipitate the magnesium and calcium as insoluble compounds.

During recent years, several new organic compounds have been introduced for use as detergents. One of these is produced in the following manner. (1) lauric acid, $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$, is treated with hydrogen and converted into lauryl alcohol, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$, (2) lauryl alcohol is then treated with sulfuric acid and converted into lauryl acid sulfate, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{HSO}_4$, (3) lauryl acid sulfate is then treated with sodium hydroxide to form so-

dium lauryl sulfate, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{NaSO}_4$. This substance and similar salts are sold under the name of *Dreft*. Substances of this kind are not soaps from a strictly chemical point of view, but they are excellent detergents. The calcium salt of lauryl acid

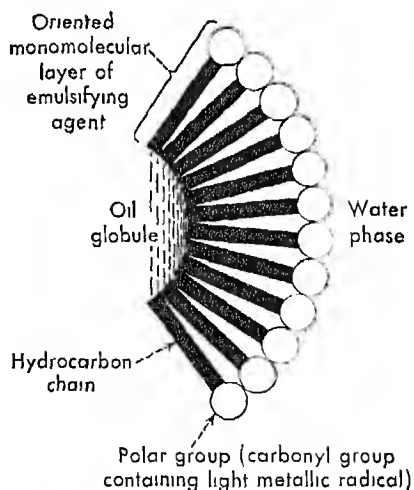


Figure 274. Diagrammatic Illustration of an Emulsifying Agent in an Oil-in-Water Emulsion Showing Soap Molecules Separating Oil and Water

sulfate is as soluble as the sodium salt, hence there is no formation of scum when Dift is mixed with hard water. It lathers equally well in cold and hot water and in soft and hard water.

DERIVATIVES OF BENZENE AND OTHER AROMATIC HYDROCARBONS

17. The Ring Structures of Benzene and Related Compounds

The ring structures of benzene and its derivatives, as shown on the next page, are based upon the chemical behavior of these substances, and also upon certain physical properties that we shall not discuss here. It has been clearly demonstrated, for example, that all six atoms of hydrogen in the benzene molecule are identical in chemical behavior. If they were not, it should be possible to produce different substances by substituting an atom of chlorine for one atom of hydrogen; different compounds would be produced, depending upon which atom of hydrogen was replaced by chlorine. There is, however, only one compound corresponding to the formula C_6H_5Cl . If the six atoms of carbon were in a chain, as they are in normal hexane, one compound would result if chlorine replaced an atom of hydrogen at an end of the chain, another compound would be produced if chlorine replaced hydrogen attached to the second carbon atom from one of the ends, and still a third compound would result by replacing hydrogen attached to the third carbon atom from the end of the chain.

Furthermore, there are *only three dichlorobenzenes*, $C_6H_4Cl_2$. If one chlorine atom replaces an atom of hydrogen in position (1) of the benzene

molecule (Figure 275), the second atom of chlorine may replace atoms of hydrogen in positions (2), (3), or (4), if substitutions occur in positions (5) and (6), the same compounds are formed as when replacement occurs in position (2) and (3). Since there are only three dichlorobenzenes, carbon atoms (2) and (6), and atoms (3) and (5) must be identically situated with respect to atom (1), atoms (2) and (6) are next to (1), and (3) and (5) are each separated from (1) by a single atom of carbon. This condition could not be true, and we could not explain the formation of *only three* dichlorobenzenes, if the six carbon atoms were joined together as a chain, in such a chain, atoms (2) and (6) could not be located identically with respect to (1).

18. Coal Tar

Benzene and toluene are recovered by washing coal gas in oil "scrubbers" (page 575). These hydrocarbons are also produced during the fractional distillation of coal tar, which also yields xylene, naphthalene, anthracene, phenol, cresols, and other substances of lesser importance. Each of these direct products of coal, or coal tar, is the starting material for the manufacture of many valuable substances. In general, these derivatives are called "coal-tar compounds." Although there are several thousand of these compounds, we can only touch upon some of the most important in this book.

19 Some Derivatives of Aromatic Hydrocarbons

Corresponding to the aldehydes, acids, alcohols, and other products of the methane hydrocarbons, benzene forms similar derivatives. Some of these are shown by the following structural formulas:

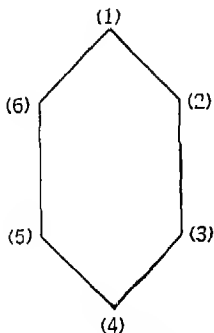
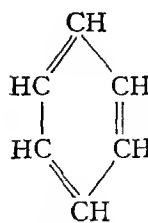
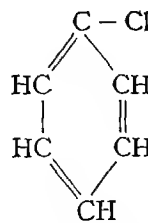


Figure 275 Positions in the Molecule of Benzene

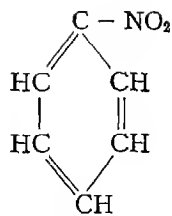


Benzene

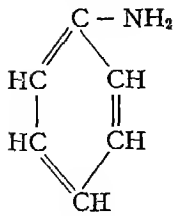


Chlorobenzene

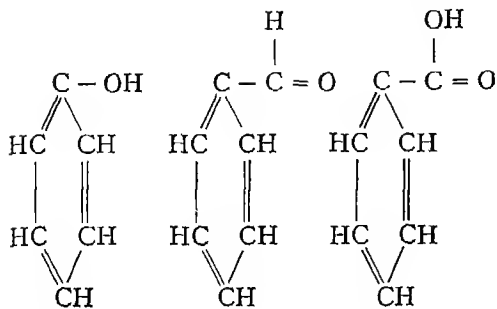
DERIVATIVES OF THE HYDROCARBONS



Nitrobenzene



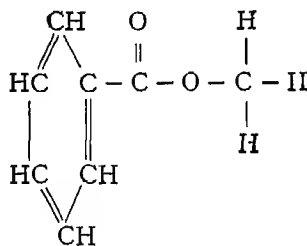
Aminobenzene (aniline)



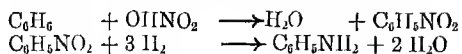
Phenol

Benzaldehyde

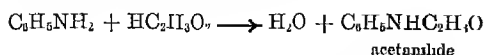
Benzoic acid

Methyl benzoate
(an ester)

Aniline is the important substance from which many dyes and drugs are produced. It is made by first allowing nitric acid to react with benzene to form *nitrobenzene*. This substance is then reduced by atomic hydrogen to form aniline.

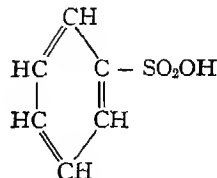


Aniline is a colorless liquid, which turns dark red upon standing. An example of its use in producing drugs is illustrated by its reaction with acetic acid to form *acetanilide*.

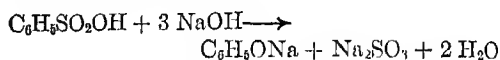


Phenol ($\text{C}_6\text{H}_5\text{OH}$) is obtained directly during the distillation of tar. It is a white, crystalline solid. It is used in making certain synthetic

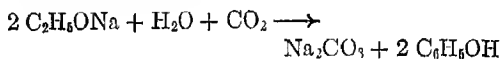
resins (page 585) and picric acid (page 487). If benzene is treated with concentrated sulfuric acid, one of the hydrogen atoms of the benzene molecule is replaced by the $-\text{SO}_2\text{OH}$ group, forming *benzene sulfonic acid*.



If this substance is fused with sodium hydroxide, the sodium salt of phenol is produced:

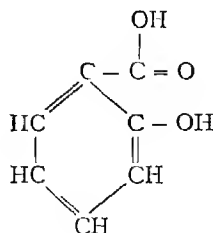


Phenol is then made from the sodium salt by the action of carbon dioxide:

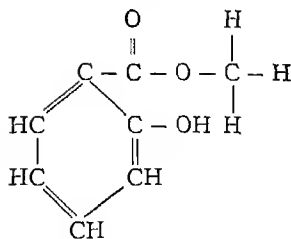


These reactions constitute an important method of producing phenol from benzene. The formation of the sodium salt of phenol in this process indicates that phenol has the properties of a weak acid. It is analogous to the hydroxides of elements such as nitrogen, phosphorus, chlorine, and arsenic. Because of its acid properties, phenol is familiarly known as *carboic acid*. It is extremely corrosive in its action upon flesh. In dilute solutions it serves as an excellent antiseptic for destroying certain forms of bacterial life.

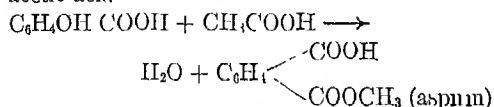
Phenol is also used to produce *salicylic acid*.



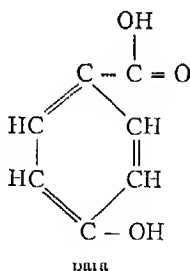
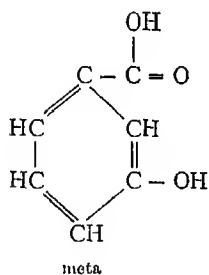
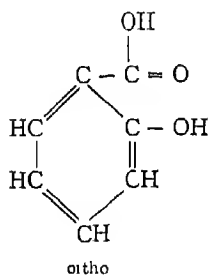
This acid is important because of its use in making *aspirin* and other drugs, also *methyl salicylate* (wintergreen). The latter is the ester of this acid and methyl alcohol.



Aspirin is *acetyl salicylic acid*. In producing this drug salicylic acid acts as an alcohol, through its hydroxyl radical, and forms an ester with acetic acid.



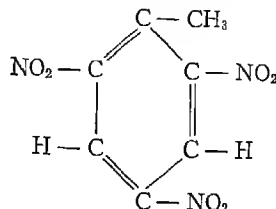
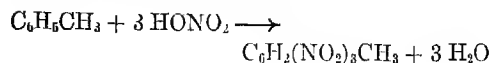
There are two other acids which are isomers of salicylic acid. These are called *meta*- and *para*-hydroxybenzoic acids. We might call salicylic acid *ortho*-hydroxybenzoic acid. The structures of these three substances are typical of many compounds in which two atoms or radicals are substituted on the benzene ring.



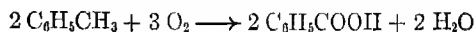
If the two substituents are attached to adjacent carbon atoms, the derivative is known as the *ortho* compound. If they are separated by one carbon atom, the *meta* isomer is formed. If they are directly across the ring from each other, the *para* isomer results. The existence of only three such isomers for any two substituents is one of

the reasons for assigning the ring structure to the benzene molecule.

Toluene is the starting material for trinitrotoluene (page 487), which is made by treating the hydrocarbon with nitric acid.

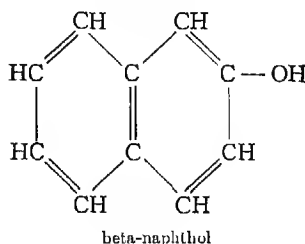
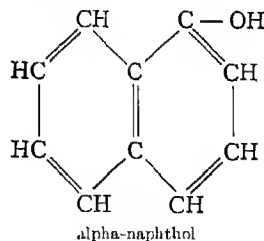


Benzoic acid is made by oxidizing toluene.



Sodium benzoate is widely used as a preservative of foods.

Naphthalene and *anthracene* are important starting materials in the manufacture of many drugs and dyes. The former is used in ordinary "mothballs." The hydroxyl derivatives of naphthalene are called *naphthols* and are used to make certain dyes. The structures of *alpha*- and *beta*-naphthol are



Review Exercises

- 1 Name the six classes of the oxygen derivatives of the hydrocarbons. What group, or radical, characterizes the compounds of each class?

- 2 Write the structural formulas of at least four isomers corresponding to the formula $C_6H_{12}OH$
- 3 Give one example each of a primary and a secondary alcohol. What products are formed when these alcohols are mildly (not completely) oxidized?
- 4 Of what hydrocarbon is glycine a derivative?
- 5 Name two ways of producing methyl alcohol. Briefly describe each method.
- 6 For what purpose is yeast added in the production of ethyl alcohol from sugar?
- 7 Write an equation, using structural formulas, to show how diethyl ether is made from ethyl alcohol, how formaldehyde is made from methyl alcohol, and how acetone is made from secondary propyl alcohol.
- 8 Enumerate some of the important uses of methyl alcohol, ethyl alcohol, ether, formaldehyde, and acetone.
- 9 Explain the changes that occur in the production of vinegar from cider.
- 10 To what group of substances does the term *fatty acids* refer?
- 11 How does the reaction of an alcohol with an acid differ from the reaction of a base with the same acid?
- 12 Write an equation to show the hydrolysis of an ester.
- 13 Write an equation for each of the following reactions: sodium butyrate and dilute sulfuric acid, palmitin and sodium hydroxide, glycerine and nitric acid.
- 14 What is the difference in composition of the liquid and the solid fats?
- 15 Describe the general nature of the chemical changes occurring in the following cases: saponification, hydrogenation of fats, when calcium acetate is heated, when fats become rancid.
- 16 Explain the cleansing action of soaps.
- 17 Write formulas for nitrobenzene, phenol, ortho nitrobenzoic acid, aniline, naphthalene, salicylic acid.
- 18 What is an alkyl group? Give two examples by names and formulas.
19. By means of structural formulas show the relationships of ethyl alcohol, acetaldehyde, acetic acid, and ethyl acetate to one another and to ethane.
- 20 An alcohol was found to contain 60 per cent of carbon and 26.67 per cent of oxygen. Upon oxidation it produced a ketone. What is its structural formula?
- 21 What volume of absolute ethyl alcohol can be produced by the fermentation of one kilogram of glucose, assuming all the glucose is used?
- 22 What weight of diethyl ether can be produced from 100 liters of absolute ethyl alcohol?
- 23 What is the percentage of carbon in palmitic acid?
- 24 A cake of soap weighs 200 g. and contains 10 per cent of water. If the soap is sodium palmitate, what weight of sodium hydroxide was required to make it?
- 25 A sample of vinegar weighed 100 g., and 60 ml of 1 N sodium hydroxide solution was required to neutralize the acetic acid in it. What percentage of acetic acid did the vinegar contain?

References for Further Reading

- Texts of Organic Chemistry: Caldwell, W. T., *Organic Chemistry*, Boston: Houghton Mifflin Company, 1943; Conant, J. B., and M. Tishler, *Chemistry of Organic Compounds*, Rev. ed., New York: The Macmillan Company, 1939; Porter, C. W., *Carbon Compounds*, 3d rev. ed., Boston: Ginn and Company, 1938; Williams, R. J., *An Introduction to Organic Chemistry*, 3d ed., New York: D. Van Nostrand Company, 1935.
- Many chapters in the following books and in other similar books contain a vast store of information presented in an interesting manner on the various subjects of organic chemistry: Slosson, E. E., *Creative Chemistry*; Howe, H. E., ed., *Chemistry in Industry*; Foster, W., *Romance of Chemistry*; Arrhenius, S. A., *Chemistry in Modern Life*.
- Alcohols: *Ind. and Eng. Chem.*, **12**, 370 (1920), **32**, 1588 (1940).
- Soap: *J. Chem. Ed.*, **2**, 1035, 1130 (1925), *Ind. and Eng. Chem.*, **21**, 60 (1929).
- Synthetic Methyl Alcohol: *Ind. and Eng. Chem.*, **20**, 285 (1928), *J. Chem. Ed.*, **2**, 429 (1925), **3**, 385 (1926).

CARBOHYDRATES AND PROTEINS: FOOD AND NUTRITION

Every fact that has been discovered about the chemistry of cellulose has led to the founding of an industry

LITTLE

CARBOHYDRATES

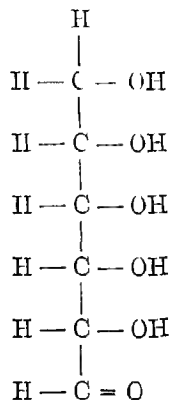
The carbohydrates are compounds of carbon, hydrogen, and oxygen in which the hydrogen and oxygen are usually present in the same proportion as they occur in water, that is, two atoms of hydrogen for every atom of oxygen. This does not mean that these two elements exist as water molecules in the molecule of the carbohydrate. The oxygen is often present as a part of a hydroxyl, an aldehyde, or a ketone group, and the hydrogen is combined directly with carbon (as in a hydrocarbon) or is a part of a hydroxyl radical. The most important carbohydrates are sugars, starch, cellulose, and substances closely related to them.

1 Sugars

Sugar is the name applied to a certain group of carbohydrates which are best known because of their sweet taste. They may be classified as *monosaccharides*, which have the empirical formula $C_6H_{12}O_6$, and *disaccharides* which have the formula $C_{12}H_{22}O_{11}$. Each group consists of several isomers. The most important monosaccharides are glucose and levulose. Sucrose, maltose, and lactose are the most important disaccharides.

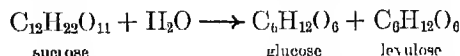
2 Glucose

This sugar is also called *dextrose* or *grape sugar*. It has the following structural formula



Glucose, therefore, possesses the structural characteristics of a pentahydric alcohol and also those of an aldehyde.

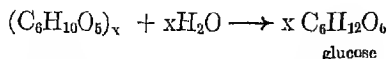
Glucose occurs in the juices of many fruits. It can be produced, also, from the disaccharides, from starch, and from wood. Thus, the hydrolysis of ordinary cane sugar (sucrose) yields glucose and its isomer, levulose.



This reaction is catalyzed by acids and, in the process of digestion, by certain enzymes. Maltose gives upon hydrolysis two molecules of glucose, lactose hydrolyzes to form glucose and galactose, which is an isomer of glucose.

When corn starch is boiled with water containing hydrochloric acid, a product

called "corn sugar" is obtained. The acid acts as a catalyst in the hydrolysis of the starch



The above equation shows the hydrolysis of starch to form glucose. The actual change in the starch is much more complex than this single equation shows, for "corn sugar" contains the disaccharide, maltose, and dextrin, which is a substance related to starch, in addition to glucose. The "corn sugar" is obtained by neutralizing the acid with sodium carbonate and evaporating the solution in which the starch is hydrolyzed. The evaporation produces a dry, hard cake, which is then pulverized. If the solution is evaporated to a concentrated state "corn syrup" is produced. This syrup is used for sweetening in baking pastries, in making candies, as a table syrup, and as a syrup for the sweetening of various soda-fountain products. It is also fermented to produce ethyl alcohol.

Glucose is now produced from cellulose by heating wood waste (sawdust) with steam under pressure and in the presence of sulfuric acid. The reaction is similar to that for starch. The glucose thus produced can be converted into ethyl alcohol. This process has been used in Germany for some time, and during World War II, a plant based upon the same process was constructed in the United States.

3. Sugar in the Body

Starch and the disaccharide sugars, such as cane sugar, are converted into glucose, or some of its isomers, during digestion. Glucose and its isomers therefore represent the digested form of most of the carbohydrates contained in our foods. Glucose passes without further change through the walls of the intestines and into the blood, by which it is carried to the various parts of the body. The blood normally contains about 0.1 per cent of this sugar. Since it is available immediately as nourishment without undergoing any of the digestive changes through which other foods must pass in the stomach or intestinal tract, a solution of glucose sometimes is injected directly into the blood of

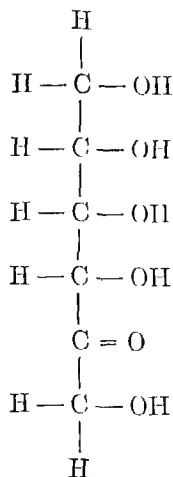
patients seriously in need of immediate nourishment and unable to take ordinary food.

In cases of the disease known as diabetes mellitus, or simply diabetes, the body becomes unable to assimilate glucose, and this sugar must then be eliminated from the blood through the kidneys. The presence of glucose in the urine is, therefore, one of the prominent symptoms of this disease.

The detection of glucose is based, usually, upon the reduction of copper from its valence of 2 to cuprous oxide in an alkaline solution. The most familiar reagent for this purpose is Fehling's solution, which is made by dissolving cupric sulfate in one solution and sodium hydroxide and Rochelle salt (page 587) in another. The two solutions are mixed just before the test is made. When a few drops of a solution containing glucose is added, and the mixture is heated, red or yellowish-red cuprous oxide is precipitated. Glucose is called, therefore, a reducing sugar. Certain other sugars also reduce Fehling's solution.

4. Levulose

This sugar is also called *fructose* and fruit sugar. It is a white solid and is several times sweeter than cane sugar. It occurs with glucose in honey and in many fruits. The structural formula of levulose is given below.



This sugar contains the ketone group, $-C=O$, while glucose, its isomer, contains the aldehyde group $-CHO$

Levulose can be produced by the hydrolysis of *inulin* ($C_6H_{10}O_5$)_x, which is a substance closely related to ordinary starch. Inulin is present in various tubers, such as dahlia bulbs, and in the Jerusalem artichoke. Considerable research has been carried out to find the most effective methods of preparing and refining the levulose made from the inulin of this artichoke. Levulose, if it could be prepared on a large scale, would be of considerable value and importance, because of its extremely sweet taste and also because it can be used by diabetic patients without aggravating their pathological condition.

5. Sucrose ($C_{12}H_{22}O_{11}$)

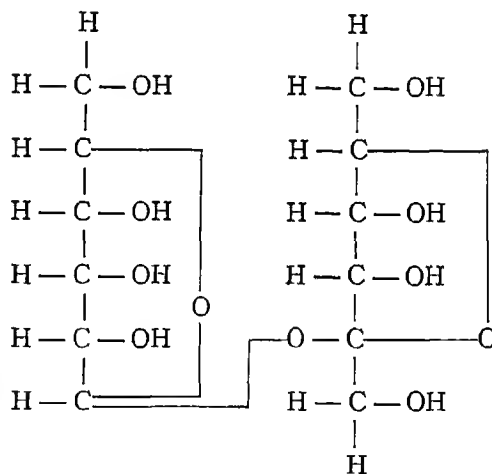
Sucrose is the most familiar sugar. Cane, sorghum, sugar beets, the sugar maple, and some fruits (pineapples and strawberries) contain sucrose. Cane and sugar beets furnish most of the world's supply. The former contains about 15 per cent and the latter about 17 per cent of sucrose.

The juice extracted from cane is evaporated in closed vessels under reduced pressure to prevent the decomposition and charring of the sugar. The crude sugar produced in the mills located near the sugar plantations is brown in color and contains many impurities. When this brown sugar reaches the refinery, it is dissolved in water, and the syrup is then filtered through beds of bone charcoal, which removes the coloring matter. Carbon dioxide is also passed into the solution to remove calcium salts. The colorless syrup is then evaporated in "vacuum pans" until crystals begin to form. The concentrated syrup is stirred as it cools, in order that small crystals (granulated sugar) may be obtained. The crystals are dried by whirling in centrifugal machines. If the sugar is allowed to crystallize slowly and quietly, large monoclinic crystals, known as rock candy, are produced. The concen-

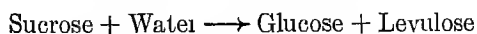
trated solution remaining after the crystals are removed contains several sugars and is used as ordinary *molasses*. Cubic sugar is made by moistening small sugar crystals and pressing them into small cubes. Contrary to a somewhat general opinion, cane and beet sugars are identical, if they are carefully purified. Sucrose is, likewise, the sugar in maple syrup and maple sugar, which owe their characteristic flavor to other substances.

Sucrose melts at about 185° . If the liquid is heated to about 215° – 220° , partial decomposition occurs, and the sugar turns brown. The product is *caramel*, which is used in making candies and as a coloring material for many foods and beverages.

Sucrose is thought to be made up of a molecule of glucose united with a molecule of levulose, a molecule of water is lost in the union.



One reason for believing that this is the structural formula of sucrose is based upon the formation of one molecule each of glucose and levulose from one molecule of sucrose, when the latter hydrolyzes in the presence of a dilute aqueous solution of an acid.



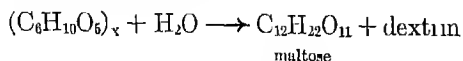
The mixture of glucose and levulose produced by hydrolysis is called *invert sugar*. The properties of invert sugar are consider-

ably different from those of sucrose. The former does not crystallize and for this reason has certain advantages in baking pastries, and in making candies, concentrated syrups, and other food products in which crystallization is undesirable. Sucrose does not reduce Fehling's solution, while invert sugar reduces it readily. Honey is largely invert sugar. The bee gathers sucrose from flowers but this sugar is inverted, before it is deposited in the comb, by the action of formic acid in the bee's body or by the action of enzymes. Invert sugar is also present in the molasses remaining after the sucrose has been recovered in the sugar refinery. Invert sugar is not so sweet as sucrose. It is also used as a moistening agent for tobacco and other products to prevent them from drying out upon standing.

When cane sugar is dissolved in water and yeast is added, an enzyme produced by the yeast cells, called *invertase*, first causes the sucrose to be converted into glucose and levulose. A second enzyme called *zymase* then acts upon the simpler sugars to form ethyl alcohol and carbon dioxide (page 583). Enzymes in the body convert sucrose into glucose and levulose during digestion.

6. Maltose ($C_{12}H_{22}O_{11}$)

Maltose is produced by the action of an enzyme called *diastase* upon starch. When barley and other grains germinate and start to grow, the starch that they contain is converted into maltose by the action of this enzyme. If the germinated grain is heated and dried, a product containing diastase and known as *malt* is produced. Malt causes starch to be hydrolyzed, thus producing a mixture of maltose and dextrin. The latter is a close relative of starch.



The product is called *dextrinmaltose*, and is used as a food for infants, in candies, and in making malted milk drinks. If yeast is added to the solution containing maltose,

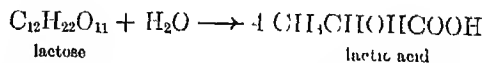
enzymes convert the maltose into glucose and the glucose into ethyl alcohol. This is the method of producing "malt liquors," such as beer.

Maltose is converted into glucose by the action of the enzyme *maltase* during digestion. The *ptyalin* in saliva starts the conversion of starch into maltose, and the production of glucose is later completed in the intestines. Maltose is a very nutritious food, since one molecule produces two molecules of glucose upon hydrolysis.

7. Lactose ($C_{12}H_{22}O_{11}$)

The only source of natural lactose is milk. Cow's milk contains about 5 per cent and human milk about 7.5 per cent of this sugar. It is commonly called milk sugar. Lactose is not so sweet as sucrose and it is less soluble in water. The slight solubility of milk sugar is responsible for the granular texture of some ice creams, because the sugar may crystallize at the low temperature at which the ice cream is prepared. The addition of gelatin furnishes a protective colloid (page 553) and prevents this condition.

When milk sours, lactose is converted into lactic acid.



This is a type of acid fermentation. It is produced by the action of a certain kind of bacteria that is always present in the air. The pasteurization of milk kills the bacteria already present, in this process of sterilization the milk is heated at a temperature of about 65° for forty to sixty minutes. Pasteurized milk must of course be kept out of contact with the air, if it is to be preserved. The object of pasteurization, however, is not to keep milk from souring but to kill typhoid bacilli and other bacteria of a harmful character that may have been present originally in the milk.

The hydrolysis of lactose yields equal numbers of molecules of glucose and galactose, an isomer of glucose. This change also

occurs under the influence of enzymes during digestion. Lactose does not ferment when yeast is added, but when milk has started to sour, the acid catalyzes the hydrolysis of lactose, and this reaction results in the formation of glucose, which does ferment when yeast is added. This principle is the basis of the production of certain fermented milk liquors, such as *koumiss*.

8 Starch and Dextrin

These substances as well as glycogen and cellulose, both of which are discussed below, are polysaccharides (page 597). The proportions of carbon, hydrogen, and oxygen in them are represented by the simple formula $C_6H_{10}O_5$, but their actual molecular weights and, therefore, their real formulas are unknown; hence, the formula of each of them is written as $(C_6H_{10}O_5)_x$, where x is a large number whose exact value is not known.

The chief source of starch in the United States is corn, in Europe it is the potato. Plants store it away in grains, tubers, and fruits as a food supply for the young plant until it has developed a leaf system of its own and can manufacture its own food. Unripened fruits contain a large percentage of starch, which is partially converted into sugar as the fruit ripens. The starch from all these sources is the same substance, but the starch granules from different grains and other sources may be distinguished by their sizes, shapes, and other characteristics.

During digestion, starch is converted into maltose. This change is begun by the action of the enzyme *ptyalin* of the saliva and is later completed by the action of *amyllopsin* in the intestines. Maltose is eventually converted by *maltase* into glucose, which passes through the intestinal walls into the blood.

Cooking causes the starch granules to burst. The starch of cooked foods is therefore more directly attacked by the digestive fluids than is uncooked starch. When dry starch is heated, it undergoes a partial decomposition and dextrin is formed. This change occurs to some extent on the surface of

toasted bread. Dextrin has the same simple empirical formula as starch $(C_6H_{10}O_5)_x$, the difference is in the value of x , which is smaller for dextrin than it is for starch. There are really several kinds of dextrin, which vary in the complexity of their molecular structure. Dextrin has a sweet taste. It is used chiefly as an adhesive on stamps, envelope flaps, and the like. Dextrin, along with maltose and glucose, is also produced when starch is boiled with water containing a little hydrochloric acid (page 598).

Starch does not dissolve in cold water. A suspension is made by boiling starch in water, and the so-called *soluble* starch is made by the action of a cold dilute solution of hydrochloric acid upon starch. When starch is treated with iodine a blue color is produced (page 342). This change is used as a simple test for both iodine and starch. The test should be made upon cold materials, as the blue color of the treated starch disappears upon heating.

The exact formula and the molecular weight of starch are unknown. It is probable, however, that the molecule contains hydroxyl groups, since starch can be nitrated by treating with a mixture of nitric and sulfuric acids. "Nitro-starch" has been used to a limited extent as an explosive.

The use of starch in the laundry is familiar to everyone, and its use in producing corn sugar and corn syrup has already been mentioned (page 598). Starch is also used in large quantities to produce ethyl alcohol, by conversion into glucose and maltose with the subsequent action of yeast, or by the action of malt and yeast (page 534).

9. Glycogen $(C_6H_{10}O_5)_x$

Corresponding to the starch of plants, animals produce glycogen as a storage food. This substance is very much like ordinary starch. It is found in the liver and in the muscles. In the latter its conversion into lactic acid accompanies the use of the muscle in physical exercise (page 80). Like starch, glycogen is hydrolyzed to form

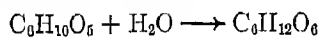
glucose. It is converted by the enzymes of the body into maltose and then into glucose.

10. Cellulose ($C_6H_{10}O_5$)_x

Cellulose has the same empirical formula as starch. Its structural formula and molecular weight are unknown. It forms the woody portions of all plant structures and is the principal substance in the wall of every plant cell. The chief sources of industrial cellulose are cotton and wood.

It is thought that the molecules of cellulose are built up in the plant by the polymerization of $C_6H_{10}O_5$ groups, which combine with one another to form a long chain. The $C_6H_{10}O_5$ group may be produced by the loss of a molecule of water from a molecule of glucose.

Cellulose can be converted into glucose by the action of hot dilute sulfuric acid. Using a single $C_6H_{10}O_5$ group, the equation for this reaction may be written as



The reaction must be carried out at high temperatures and under pressure. Similar changes do not occur in digestion, and the cellulose contained in food is unused. Some of the smaller forms of animal life appear to be able to digest it. The decay of wood is probably hastened by the action of the enzymes produced by certain organisms. The enzymes produce a partial hydrolysis of the cellulose.

The molecule of cellulose contains hydroxyl radicals and reacts, therefore, with nitric acid, and other acids, to form esters (page 588). The moderate action of a mixture of nitric and sulfuric acid produces *cellulose nitrate*, which contains from 10 to 12 per cent of nitrogen. This is the product known as pyroxylin (page 485). More nearly complete nitration yields an ester which contains up to 13.5 per cent of nitrogen. This product is called gun cotton (page 485). The two substances may be distinguished and separated by taking advantage of the solubility of pyroxylin in a mixture of

ether and alcohol, in which gun cotton is insoluble.

Gun cotton is used chiefly in producing explosives, such as smokeless powders, cordite, and gelatin dynamites. Pyroxylin is used in the manufacture of photographic film, lacquers, artificial leather, celluloid or pyralin, and collodion. When used as a base for modern lacquers, cellulose nitrate is dissolved in a volatile solvent such as amyl acetate. Artificial leathers are made by impregnating canvas cloth with solutions of cellulose nitrate. This fabric is used as coverings for automobile seats, for the upholstering of furniture, and in making book bindings, luggage, window shades, screens, and the like. Collodion is prepared by dissolving cellulose nitrate in a mixture of alcohol and ether. Celluloid is prepared by making a plastic mass of cellulose nitrate, camphor, and alcohol. The mass is pressed into blocks by means of hydraulic presses which are operated at moderately high temperatures.



Courtesy of du Pont Company

Figure 276 Processing Nitrocellulose in the Manufacture of Pyralin

The material is forced through a fine screen sieve by hydraulic pressure to take out foreign matter.

Upon cooling the material becomes hard and is then cut up into sheets of the desired thickness. Different colors, mottled effects, and imitations of ivory, horn, mother of pearl, and other materials are secured by adding the proper coloring materials.

11. Other Reactions and Products of Cellulose

Vulcanized fiber is prepared by treating sheets of pure unsized paper with a hot solution of zinc chloride. The sheets are rolled up on large heated cylinders and pressed together to make a product of the desired thickness. The zinc chloride must be removed by washing. When dried, the vulcanized fiber is very hard, and can be sawed, turned, and threaded. It is used to make trunks, gears, washers, valves, handles, waste-paper baskets, buckets, etc.

The *lamp filaments* used in the old type of electric lamps were prepared by making a viscous liquid mixture of cellulose (cotton) in a solution of zinc chloride. This mixture was forced through very small openings into a precipitating bath, and the filaments were washed and carbonized by heat in the absence of air. Filaments of very finely drawn tungsten are now used in place of carbon.

Oxalic acid can be made by heating wood chips or sawdust with sodium hydroxide. After heating, the mixture is treated with water, filtered, and the filtrate is evaporated. The residue consists of crystals of sodium oxalate, which is converted into oxalic acid by treatment with sulfuric acid.

12. Mercerization

Cotton cloth is made stronger and more durable by a process called mercerization, which involves treating the cloth with a solution of sodium hydroxide. Natural cotton fibers are twisted, flat, and shiveled. During the treatment with sodium hydroxide, the cellulose is partially hydrated and the threads are filled out, becoming straight and round. Mercerized cotton has a smoother, softer texture than cloth made from untreated cotton.

13. Paper

The average citizen of the United States uses about 250 pounds of paper per year,

and about 9,000,000 tons of wood pulp are used annually in the paper industry. The paper for newsprinting and the cheaper grades for other purposes are made from wood, but cotton rags, straw, and similar materials are also used.

To prepare wood for paper-making, it must be chipped and then treated chemically to dissolve the *lignin*, which binds together the fibers of cellulose in the natural wood. Young plants and the growing tips of older plants are more tender and more easily chewed, for example, than older twigs and branches. This is because the woody part of the plant is at first almost pure cellulose, but later develops into ligno-cellulose, which in paper-making must be reconverted into pure cellulose by chemical treatment. Calcium bisulfite is usually employed for this purpose. The chips are cooked in a solution of this substance until the lignin is dissolved and the fibers are thoroughly separated. The pulp is then washed with water and bleached with chlorine water or a solution of calcium hypochlorite.

This bleached material is poured upon one end of a moving screen, made of wire cloth, which acts as a filter and allows the water to drain through it, leaving the cellulose fibers enmeshed in the form of a wet, thick sheet of raw paper. At the other end of the screen, this sheet passes between two large cylinders. It then passes between other sets of cylinders which remove the water by pressure. The paper is finally dried by passing between cylinders which are heated by steam on the inside. Many substances, such as clay, rosin, dextrin, glue, aluminum silicate, barium sulfate, alum, and pigments or dyes are added to the pulp in producing paper of special properties. The materials added depend upon the desired color, texture, weight, and degree of opacity. Rosin, for example, makes the paper resistant to ink, and prevents spreading. Starch, glue, dextrin, and similar materials are used as "sizing" to fill up the spaces between the cellulose fibers and to give a smooth finish.

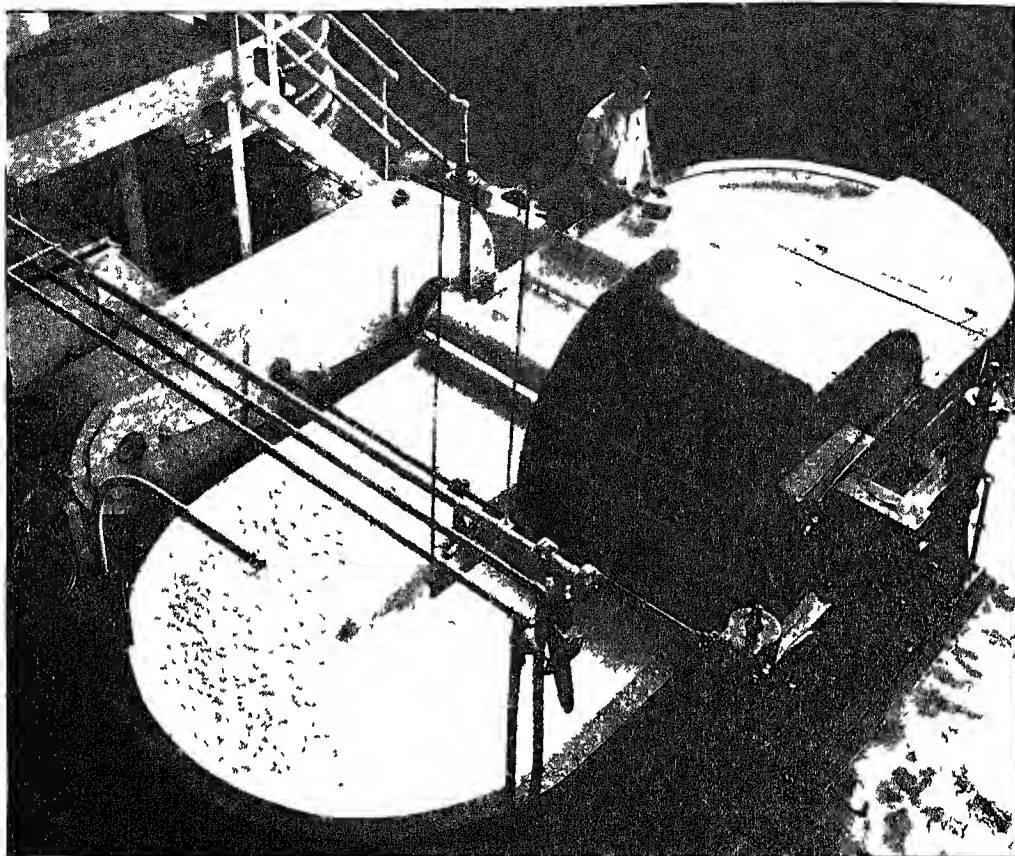


Figure 277 A Beater in Which Cellulose is Prepared for Use in Manufacturing Paper at Kodak Park

PROTEINS

14 The Chemical Nature of Proteins

In addition to fats and carbohydrates, the food of man must contain certain complex compounds of nitrogen called proteins. These substances are abundant in many plant products and are especially abundant in the bodies of animals and in animal products, such as meat, eggs, and milk. Proteins constitute the essential part of every cell associated with living things. The *casein* of milk, the *hemoglobin* of blood, the *albumen* of eggs, and the *gluten* of flour are familiar examples of proteins.

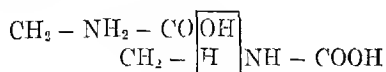
In addition to nitrogen all proteins contain carbon, hydrogen, and oxygen. Many of them also contain sulfur and phosphorus, in some, other elements, such as iron, are present. The exact

chemical character of these substances has not been determined. It is known, however, that their molecular constitution must be very complex and that their molecular weights are very large. Upon decomposition they yield *amino acids*, and this fact is responsible for the opinion that the combination of such acids with one another brings about the building up of proteins in plants and animals, or at least that the final product is a substance which may be regarded as such a compound. The amino acids contain the $-\text{NH}_2$ (amino) radical. Thus, one of the simplest amino acids is *glycine*, or *aminoacetic acid*, in which the $-\text{NH}_2$ group replaces a hydrogen atom of the methyl radical.



The amino radical is derived from the molecule of ammonia by replacement of a hydrogen atom $\text{H} - \text{NH}_2$. The acid, therefore, possesses the

basic properties of ammonia and also the acid properties which accompany the presence of the carboxyl group with its ionizable hydrogen atom. The amino acid is consequently an amphoteric substance. For this reason two amino acids might combine



This combination might be continued, of course, until it included a very large number of amino acid molecules. It is thought that this mechanism should result in the formation of substances which are proteins or like proteins in composition and character. Actual proteins are undoubtedly more complex, however, than the products which would result from the reaction shown above. We know that the hydrolysis of a single protein yields several different amino acids. At least twenty of these acids have been identified as products of the decomposition of proteins.

15 Digestion of Proteins

During digestion, proteins are acted upon by the enzyme *pepsin* and the digestive fluids of the stomach and are changed into *peptones* and *proteoses*. In the small intestine other enzymes help to hydrolyze the peptones and proteoses, converting them into amino acids. One of the enzymes of the intestines is *trypsin*. The amino acids pass through the intestinal walls into the blood, by which they are carried to all parts of the body for use in building up the complex proteins found in the bodies of all animals. The oxidation of proteins in worn-out tissues or of serum albumin in the cells produces urea, $\text{CO}(\text{NH}_2)_2$, uric acid, and other nitrogenous compounds that are eliminated from the body in urine.

16 Kinds of Proteins

The proteins are divided into several classes depending upon their composition, solubility, or general chemical properties. The *phosphoproteins*, of which the *casein* of milk is an example, contain phosphorus. The *albuminoids* are very slightly soluble proteins, *collagen*, a protein found in the bones and in the cartilage attached to them, belongs to this group. *Gelatin* and *animal glue*

are produced from collagen by hydrolysis. The *albumans* are soluble in water, members of this group are present in blood serum and in milk. The *globulins* are proteins that are not soluble in water but are soluble in salt solution or in solutions of alkalis. The *keratins* are proteins that occur in wool, hair, feathers, finger nails, hoofs, and similar animal materials. *Fibrinogen* is another blood protein, when blood clots, it is changed into *fibrin*. This change, and therefore clotting, can occur only outside the circulatory system of veins, arteries, and so on. *Hemoglobin* is the protein of the red blood corpuscles.

FOOD

A diet consisting of pure fats, carbohydrates, and proteins will not maintain health or even life for very long. Certain other substances are required. Strictly speaking, water and oxygen are foods, if by foods we mean the substances that the body requires, from external sources, to maintain life, activity, and growth. Minerals are also necessary to supply, among other things, the calcium and phosphorus from which the calcium phosphate of the bones is made, and salts, to supply chloride ion for the hydrochloric acid of the gastric fluid. All of these substances, however, do not make a satisfactory diet, unless they contain small amounts of substances called *vitamins*, which are necessary for health.

17 Vitamins

Vitamins are usually present in sufficient quantities in the diet of persons eating the ordinary kinds of food: vegetables, meat, milk, eggs, bread, cereals, and fruits. For infants who are fed prepared foods, and for adults whose diet, for one reason or another, is deficient especially in vegetables, milk, and fruits, they must sometimes be supplied.

Because of the extremely small amounts of the vitamins in foods, their recovery by extraction from such materials is not easy. Although we have learned a great deal about them in recent years, there is still much to

learn, and at the present time it is impossible to say just how many exist. Each of the known vitamins is represented by a letter, but as more and more of them are synthesized and their chemical compositions and structures are made known, their chemical names are coming more into use. Each of the vitamins is present in many plant and animal products.

Vitamin A promotes the normal growth and development of the body. The lack of this vitamin in the diet causes a disease of the eye and eventually death. It is also active in preventing infections. It is said that this vitamin has been prepared in the pure state from the coloring material of carrots. It is present in milk, butter, spinach, lettuce, and green vegetables of all kinds. It is often supplied in the form of cod-liver oil to supplement the diet of children or others who appear to suffer from a deficiency. This vitamin is sometimes referred to as a *fat soluble* vitamin, because it can be removed from the materials in which it occurs by means of solvents that dissolve it along with fats. It has been produced in pure form from certain fish oils and from the compound called *carotene*, which is found in carrots. During digestion carotene is converted into vitamin A.

The *Vitamin B Complex* consists of several different substances. *Vitamin B₁* is *thiamin hydrochloride*, which is regarded as essential for the prevention of the disease known as *beriberi* and of certain disorders of the nervous system. It is abundant in all whole cereals, in many vegetables, and in yeast. It is also produced synthetically. *Vitamin B₂* aids in the metabolism of carbohydrates and in the prevention of infections by bacteria. It also promotes the normal, healthful condition of the skin. It is abundant in milk, vegetables, and eggs. The synthetic form of this vitamin is known as *riboflavin*. *Nicotinic acid* is also a member of the B complex.

Vitamin C prevents the disease known as scurvy. It is abundant in oranges, lemons, tomatoes, and certain green vegetables, such as cabbage, lettuce, and spinach. This vitamin has been produced by synthesis and is known as *ascorbic acid*.

Vitamin D has been extracted and purified. It is the vitamin which is so essential to the normal development of the bones of children, and it pre-

vents the disease known as rickets. It is abundant in oranges, milk, and cod-liver oil. Exposure to ultraviolet light converts the substance *ergosterol* into vitamin D. Since ergosterol is present in the skin, the ultraviolet rays of the sun are beneficial in increasing the quantity of this vitamin which is available for the body's use. Certain food products containing ergosterol are sometimes irradiated before use to increase their content of vitamin D. There are several forms of this vitamin.

Vitamin E prevents sterility of man and animals and aids in the development of the young before the time of birth. It is present in meat, lettuce, and oils of vegetable origin. The synthetic vitamin is known as *alpha tocopherol*.

Vitamin K, contained in green vegetables, egg yolk, and tomatoes, aids in preventing hemorrhage. It has been produced synthetically.

18 The Functions of Food

The mineral constituents of food are required for the formation of the solid portions of the body's structure, as the bones and teeth. The vitamins are necessary to health and to the normal growth and functioning of many parts of the body. Fats and carbohydrates are oxidized and serve as a source of heat for the maintenance of the body's temperature and also as providers of muscular energy. If these substances are not present in sufficient quantities in the food which we eat, materials stored in the body, including fats and glycogen, are called upon as reserves to fill the need. Proteins may also be oxidized and to some extent will replace fats and carbohydrates in supplying energy. But the chief function of protein is to supply the material required for growth and for the replacement of worn-out tissues.

The *caloric value* of food is of considerable importance, since this is a measure of the energy which is released when the food is oxidized in the body. The caloric value of food has the same meaning as the caloric value of a fuel, namely, the heat evolved when one gram of the substance is burned. The production of heat in the body is due mainly to the oxidation of carbon and hy-

drogen to carbon dioxide and water. The average energy requirement is between 2,000,000 and 3,000,000 calories per day. A very active person engaged in manual labor requires more than 4,000,000 calories

daily. The average diet should contain about 65 to 75 grams of proteins per day.

The composition and caloric value of some of the common food-stuffs are given in Table 34.

TABLE 34

Composition and Caloric Value of Food Materials *

(Values are given in approximate per cent or as approximate number of calories per pound)

Food	Water	Fat	Carbohydrates	Protein	Calories per pound **
Eggs	74	10		13.5	675
Cereals (Oatmeal, rice, etc.)	75	0.5	16	3	400
Cheese	30	35	0.4	29	2,000
Potatoes	75	0.5	20	2.5	450
Beef	60	20		18	1,200
Ham	50	20		23	1,250
Bread (white)	35	1.5	52	9	1,200
Milk	83	4	5	3.5	300
Butter	14	85		1	3,500
Peas	75	3	15	7	500
Lettuce	95	0.2	3	1	90
Bananas	75	0.5	20	1.5	450
Fish	70	8		20	800

* Since the composition and the caloric value of any kind of food material varies with the individual sample, the values given above must be considered as representative of the relative amounts of the four classes of food materials to be found in some of the common kinds of foods. They are not the results of any one analysis.

** The unit of heat used in this table is the large calorie (1 Cal = 1000 calories).

Review Exercises

- How do glucose and levulose differ as regards the structure of their molecules?
- Describe two methods that can be used to produce glucose (in an impure state) from starch.
- What happens to starch and sugars during the digestive process?
- What are the sources, or methods of producing, sucrose, maltose, and lactose?
- Explain the chemical nature of each of the following: corn sugar, invert sugar, dextrose, dextrin, and dextrinallulose.
- What is malt? How does it affect starch?
- Explain Pyroxylin, glycogen, mercerized cotton, lignin, pepsin, casein, peptone, amino acid, and caloric value of food.
- Critique the following diet: eggs, fish, cheese, lettuce, and bananas.
- In what respects is milk a better diet, in itself, than potatoes or beef?
- What weight of each of the following substances will produce 2500 Calories (1 Cal = 1000 calories): milk, white bread, butter, lettuce, potatoes?
- What evidence indicates that starch and cellulose contain hydroxyl groups?
- Carbohydrates and fats are both composed of carbon, hydrogen, and oxygen. What are some of the differences in their structures or atomic groups?
- Give the names of two monosaccharides, three disaccharides, and three polysaccharides.

References for Further Reading

(See also the references for Chapter 37.)

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OTHER NATURAL AND SYNTHETIC PRODUCTS

*I must tell you that I can make urea without the
need of kidneys or of any animal whatever*

WOHLER IN A LETTER TO BERZELIUS

1. Introduction

In the preceding chapters that dealt with organic compounds we have discussed from time to time several synthetic products. In this chapter we wish to describe briefly additional products of this kind. Many of these are the results of fairly recent research and industrial developments. A few naturally occurring substances of importance, especially in medicine, are included in our discussion.

SYNTHETIC RUBBER HIGH POLYMERS

2. High Polymers

Many substances, some natural and some synthetic, owe their special properties to structures consisting of long chains of the same, and sometimes different, atom-groups linked together to form very large molecules. We have already mentioned relatively simple cases of polymerization in the discussion dealing with the molecular structures of hydrogen fluoride (page 351) and water (page 126). In the former, $(\text{HF})_2$ and $(\text{HF})_6$ molecules are produced when simple HF molecules are linked together by the formation of co-ordinate covalent bonds between the hydrogen atom of one molecule and the fluorine atom of another. Water is polymerized by the formation of bonds between the hydrogen and oxygen atoms of different molecules.

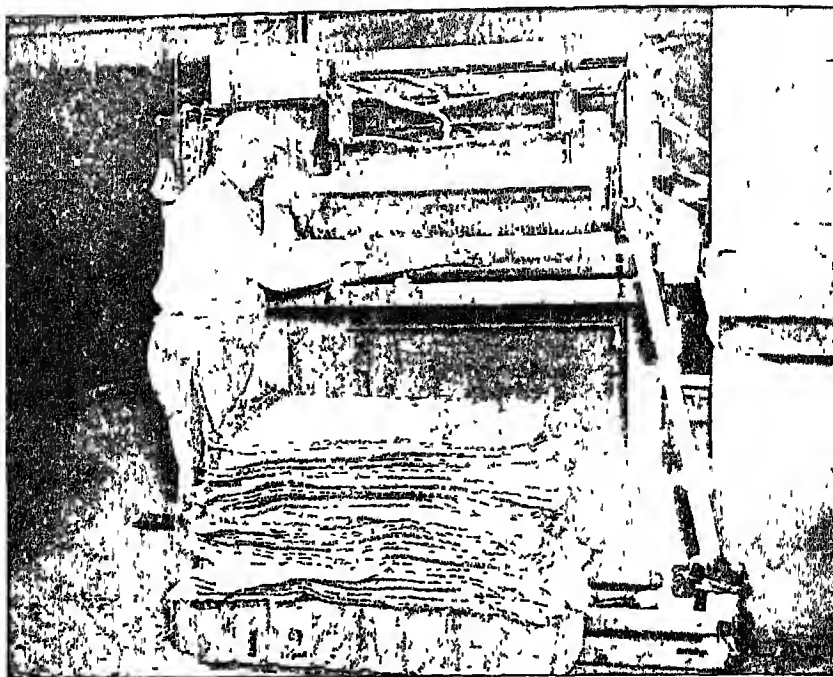
However, we refer now to much more extensive polymerization, in which many hundreds or thousands of simple molecular units are linked together. Such substances are called *high polymers*. If two different kinds of units are linked together the product is called a *co-polymer*. Those produced by the polymerization of only one kind of unit are sometimes referred to as *monomers*.

Rubber and cellulose are naturally occurring high polymers. The so-called synthetic rubbers are also high polymers.

3. Synthetic Rubber

The United States Bureau of Standards has studied the properties of 29 different "synthetic rubbers." These are, in general, not kinds of real rubber that are synthesized from different materials, but rubber-like substances that have similar properties and can be used for similar or the same purposes as rubber. The production of these "synthetics" in the United States during 1940 was 11,000 tons, and during 1944-45 it reached almost 1,000,000 tons, owing largely to the great demands for "synthetics" to replace the natural rubber that could not be imported during the war. Synthetic rubbers are also referred to as *elastomers*.

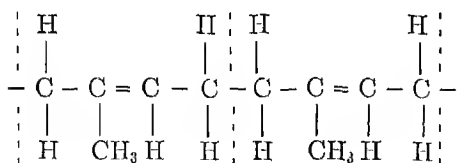
The relation of isoprene to rubber was discovered by studies of the substances produced when rubber is decomposed. These



Courtesy of The Goodyear Tire and Rubber Company

Figure 278 Buna Type Rubber Leaving the Mixer after Initial Compounding with Other Substances

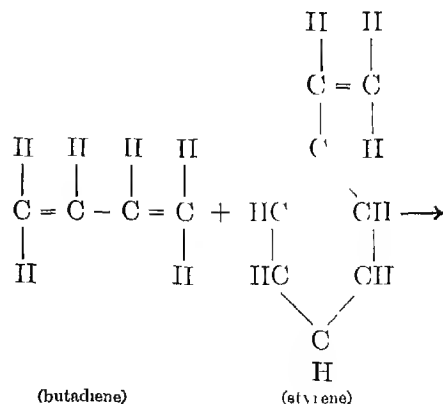
studies indicated that rubber is composed of very large molecules made up of many isoprene units joined together—polymerized—as follows

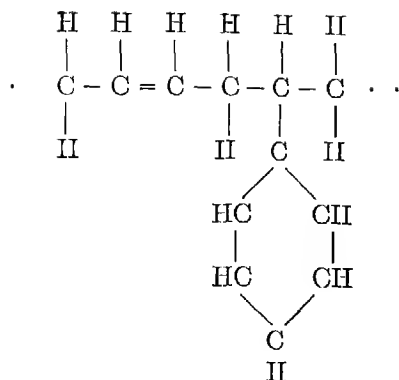


We now know that isoprene can be made to polymerize, thus forming rubber, but the difficulty in producing synthetic rubber by this process lies in the problem of making isoprene economically. This substance can be made from turpentine, from amyl alcohol, and from pentane, but none of the processes by which it can be made are able to compete successfully with natural rubber or with certain rubber-like materials made from other compounds. We shall, at this time, discuss a few of the materials that have been

most widely used as substitutes for natural rubber.

Buna S is the name given to the synthetic rubber that was produced and used most extensively during World War II. It is produced by a catalyzed reaction of *styrene*, C_8H_8 , with *butadiene* (page 568), in which these two substances polymerize together (co-polymerize) to form long chain-molecules as indicated below.





In the chain other groups identical with those shown in the equation lie on at the points indicated by the dotted lines. The butadiene used in this process is produced from alcohol or from unsaturated hydrocarbons obtained during cracking operations (page 568)

Buna N is made by the co-polymerization of butadiene and *acrylonitrile*, $\text{H}_2\text{C} = \text{CH}(\text{CN})$. *Butyl* rubber is produced from butadiene and *isobutylene* (page 568)



Courtesy of du Pont Company

Figure 279 Production of Neoprene
The synthetic rubber is being poured from a polymerization kettle

Neoprene is produced by the polymerization of a chlorine derivative of isoprene, $\text{CH}_2 = \text{C}(\text{Cl}) - \text{CH} = \text{CH}_2$, which is produced from acetylene. The acetylene, in turn, is made from limestone, coke, and water. This rubber substitute possesses qualities that make it more desirable for some purposes than natural rubber, for example, it is not disintegrated by oils. It can be used to produce many articles, including tires, ordinarily made from natural rubber, but it is more expensive than rubber in peacetime and costs more to manufacture than Buna in wartime. Neoprene is an American product made possible by the research of Nieuwland and Carothers.

Thiokol is a rubber substitute made from ethylene dichloride and the polysulfide of sodium.

PLASTICS

The term *plastic* is applied to any material which, under pressure, can be given a definite form or shape that is retained after the pressure is removed. Clay, beeswax, and pitch are natural plastics. So, too, are the resins found in the gums that exude from breaks in the bark of certain trees. Because they resemble plant resins, synthetic plastic materials are sometimes called *synthetic resins*.

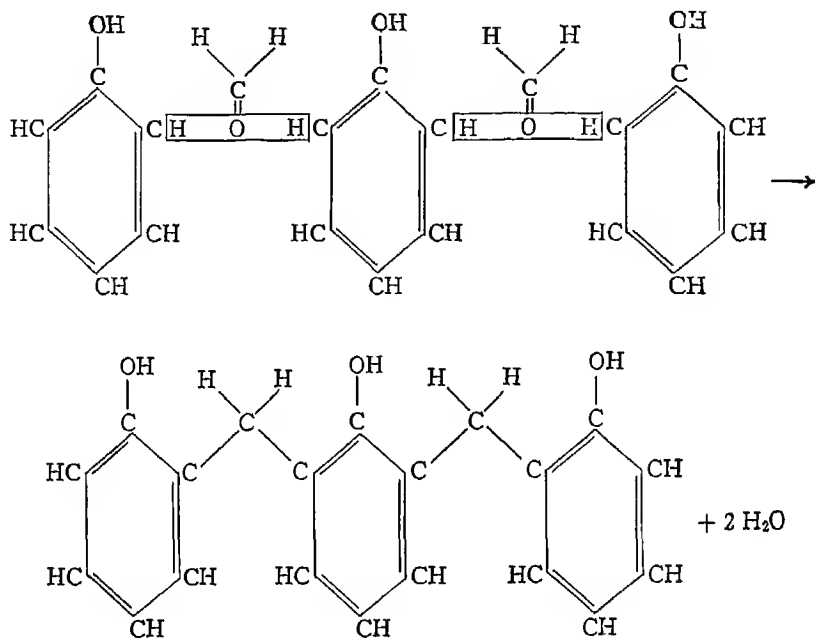
Among the first synthetic plastics produced were certain materials containing cellulose nitrate and acetate. *Celluloid* (page 602) is a plastic of this kind. These plastics are softened by heat, and when they are in this state, they can be molded into any desired shape. For this reason they are classified as *thermoplastics*. Others, when heated and then molded while still soft, set to a hard mass that does not melt or soften when heated again, these are called *thermosetting* plastics.

4 Formaldehyde-Phenol Plastics

Probably the most extensive use of formaldehyde at the present time is in the manufacture of plastic materials, or *synthetic resins*. *Bakelite*

and *Resinor* are two trade names given to synthetic plastic products which are manufactured from formaldehyde and phenol (carbolic acid). Formaldehyde and phenol are mixed in the proportion of one molecule of the former to two molecules of the latter. Many molecules of

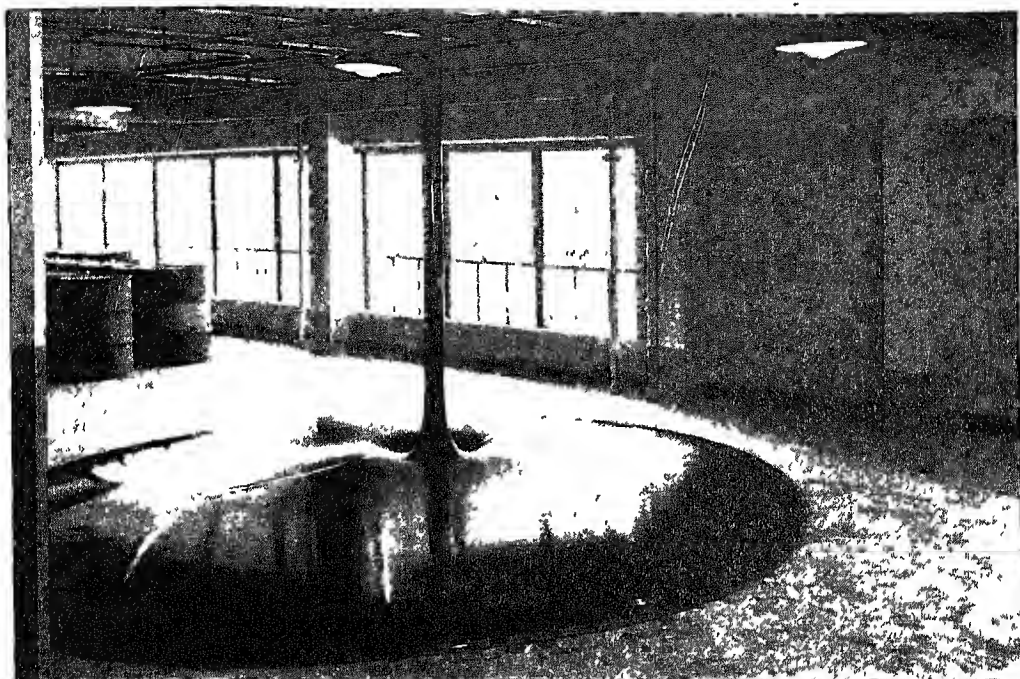
phenol and formaldehyde combine to form polymers as indicated below, water molecules are removed as shown, and phenol molecules are joined together (in three-dimensional space) in large numbers by the carbon atoms that originally belonged to molecules of formaldehyde.



If the reaction is carried out in the presence of an acid catalyst and at moderately high temperature, the product is a resinous material that can be softened or melted and is soluble in certain organic solvents. Further treatment with more formaldehyde, under increased temperature, and in the presence of a basic catalyst, gives a form of bakelite that is insoluble and does not soften when heated even at temperatures where it begins to burn. Both kinds of synthetic resin find many uses. The fusible variety is dissolved in suitable solvents, and the solution is used as a lacquer for metals. When the lacquered metal is heated, the solvent evaporates and the lacquer coating becomes hard. Paper and canvas cloth are impregnated with a similar solution of bakelite. When these are heated with steam, under pressure, they become hard. Such materials, when built up to include several layers, are used to make gears and other automobile parts, as a substitute for hard rubber, panel board, and for

many other purposes. Molded forms and articles of many different kinds are made from the synthetic resin to which are added asbestos, finely divided or powdered wood, and other fillers. These products are hard, durable, and do not soften when heated. They come from the molds with a highly polished, glossy finish. They are also good electrical insulators. Some of the articles manufactured in this manner are combs, pipe stems, pens, pencils, handles for brushes, billiard balls, phonograph records, and the insulating framework of many electrical devices, such as sockets, rheostats, switch blocks, push-buttons, telephone receivers and transmitters, and many automobile accessories and pieces of equipment.

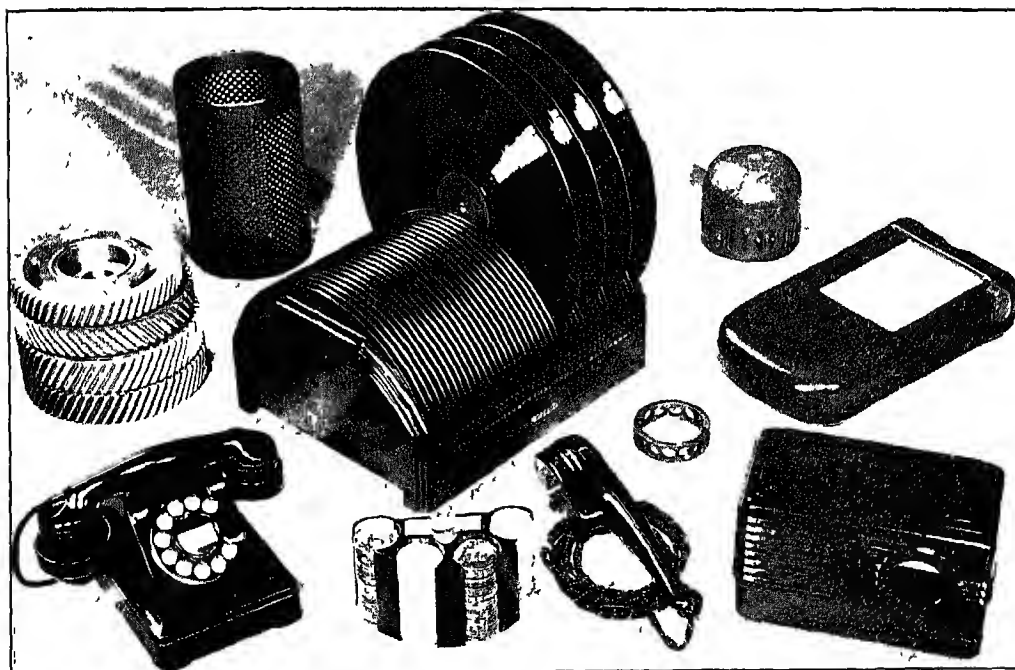
Other plastic materials are produced from formaldehyde and casein (milk curds), gelatin, albumen, and urea. The plastic material made from casein is inexpensive but it cannot be molded easily, and the articles made from it must receive a final polishing.



Courtesy of Monsanto Chemical Company

Figure 280 Formaldehyde-Phenol Plastic

The plastic is poured out on the cooling floor. After solidifying, it is broken up and ground to a powder from which are molded finished plastic articles.



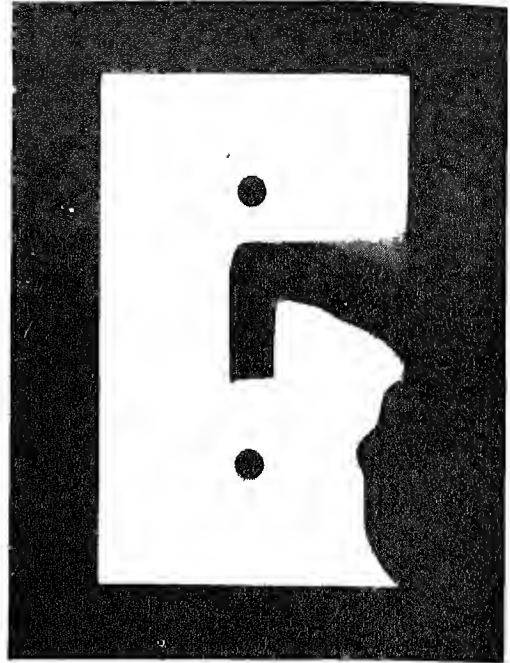
Courtesy of Koppers Company

Figure 281 A Group of Articles Made of Bakelite



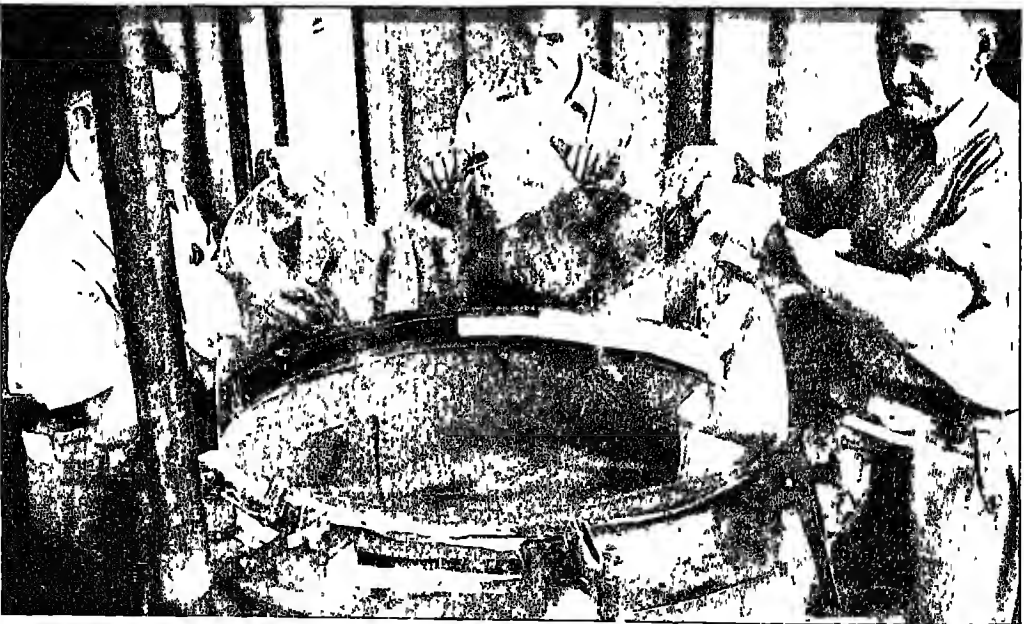
Courtesy of du Pont Company

Figure 282 The Nose of a Bomber Made From Lucite Acrylic Resin



Courtesy of du Pont Company

Figure 283 Plastic Light Switch Plate
This plate, made of Lucite Acrylic Resin, was photographed in the dark



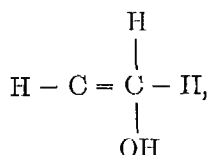
Courtesy of Rohm and Haas Company

Figure 284. Plexiglass Sheets Being Molded

Thoroughly limp and flexible after being heated to a temperature of 200 F–300 F, the plexiglass sheets are clamped between a Masonite die-stock ring and the top flange of the vacuum pot

5 Vinyl Plastics

These important plastic materials, sometimes called the *vinyl resins*, are produced by the polymerization of *vinyl alcohol*,



or certain substances closely related to it, such as vinyl chloride and vinyl acetate. In some of these plastics, two such substances are co-polymerized.

The vinyl plastics are odorless, tasteless and non-poisonous. They are used in water-proofing cloth, as a coating on the inside walls of tin cans, and as electrical insulation. They can be used to join sheets of different metals, and between two sheets of glass to make the "safety glass" used in the windshields and windows of automobiles. They are also used to manufacture cups, dishes, and many similar articles.

6 Other Plastics

The *Acryloid resins* are made by the polymerization of methyl methacrylate, the methyl ester of methyl acrylic acid, $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{COOCH}_3$. These plastics are clear and colorless. They can be molded, sawed, and tooled. They are used to make lenses and prisms for optical instruments. There are several resins in this group, the one known by the trade name of Lucite is representative of the group. Light introduced at one end of a rod made of Lucite is transmitted through the rod and comes out at the other end, although the rod may be bent one or more times at right angles.

The *polystyrene* plastics are made by the polymerization of styrene (page 610). These are light, resistant materials and are used in the manufacture of many articles such as dishes and bottles.

Phthalic acid plastics, or resins, are made from phthalic acid, $(\text{HOOC})_2\text{C}_6\text{H}_4$, and glycerine or glycol. They are sometimes referred

to as *glyptal* resins and also as *alkyd* resins. In some of them phthalic acid is replaced by another polybasic organic acid.

Rubber, and all the so-called synthetic rubbers such as Neoprene, Buna, and Thiokol, may be classified as plastics. So, too, are certain substances derived from rubber.

More and more uses for plastics are being found. It is said that the modern airplane of the bomber type contains 120 or more plastic parts, including the nose of the plane. Whole airplane bodies, ear fenders, furniture, door knobs, drinking glasses, spectacle lenses, cigarette cases, radio cabinets, telephone receivers, buttons, cooking utensils and moving picture films are but a few of the countless articles that have been or are being made from different plastics.

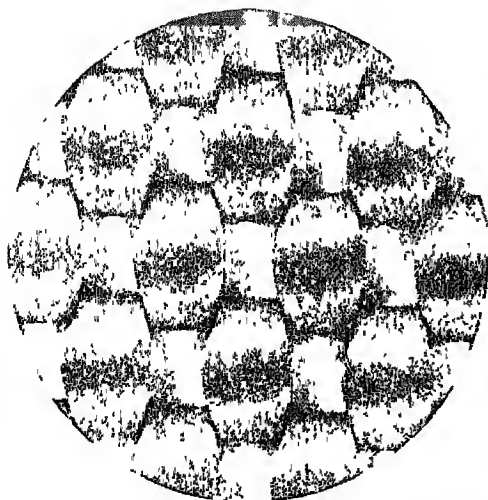
FIBERS AND CLOTH

Cotton and linen are made from vegetable fibers and are composed of cellulose. Wool is an animal fiber composed of proteins called



Courtesy of du Pont Company

Figure 285 Unloading a Shredding Machine Used to Prepare Cotton Linters and Wood Pulp for the Manufacture of Rayon



Courtesy of du Pont Company

Figure 286 Surface of a Rayon Fabric Greatly Magnified

keratins Silk, another animal fiber, is also composed of protein

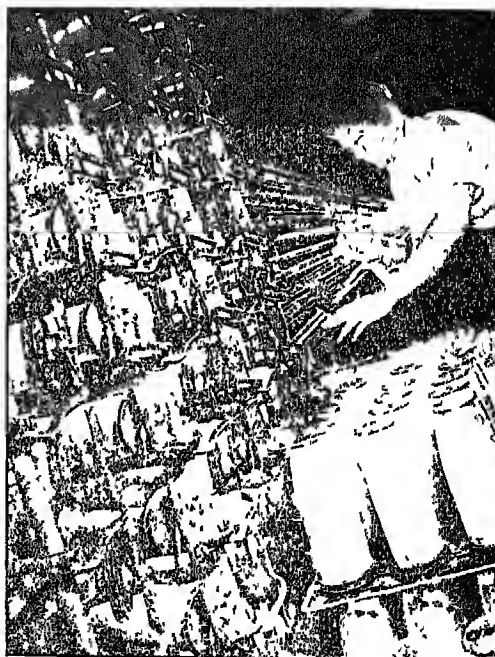
Several kinds of synthetic fibers that can be woven into cloth are now widely used. For example, a substitute for wool has been made from the protein found in casein. *Rayon* and *Nylon* are also synthetic materials

7 Artificial Silk

Probably the most widely known kind of artificial silk is *Rayon*. It is similar to silk in texture and certain other physical properties, but unlike silk in composition. Silk is an animal fiber consisting of nitrogenous substances, rayon is a form of cellulose. There are several processes for producing artificial silk, but in all of them the essential principle involves the formation of a colloidal dispersion of cellulose, or some compound made from cellulose, in a liquid. The liquid mixture is then forced through small openings in a platinum disc or nozzle into a bath containing a reagent which causes the cellulose to form again in its solid state. Since the solution enters the precipitating bath in a small stream, the cellulose forms a very small thread.

Rayon is made by the *viscose* process. Cellulose from wood pulp and from cotton is first cleaned and bleached, and then it is treated with a concentrated solution of sodium hydroxide. It is next treated with carbon disulfide, which converts it into a gelatin-like material, which forms a colloidal dispersion when mixed with a solution of dilute sodium hydroxide. This mixture is used to make the threads, which are precipitated as the liquid is forced through the small openings of a nozzle into a bath of dilute sulfuric acid and sodium bisulfate. The threads produced from one nozzle are gathered together and twisted into a larger thread, which is used in producing rayon fabrics. *Cellophane* is made in the same manner, but the cellulose is precipitated in the form of thin sheets instead of threads.

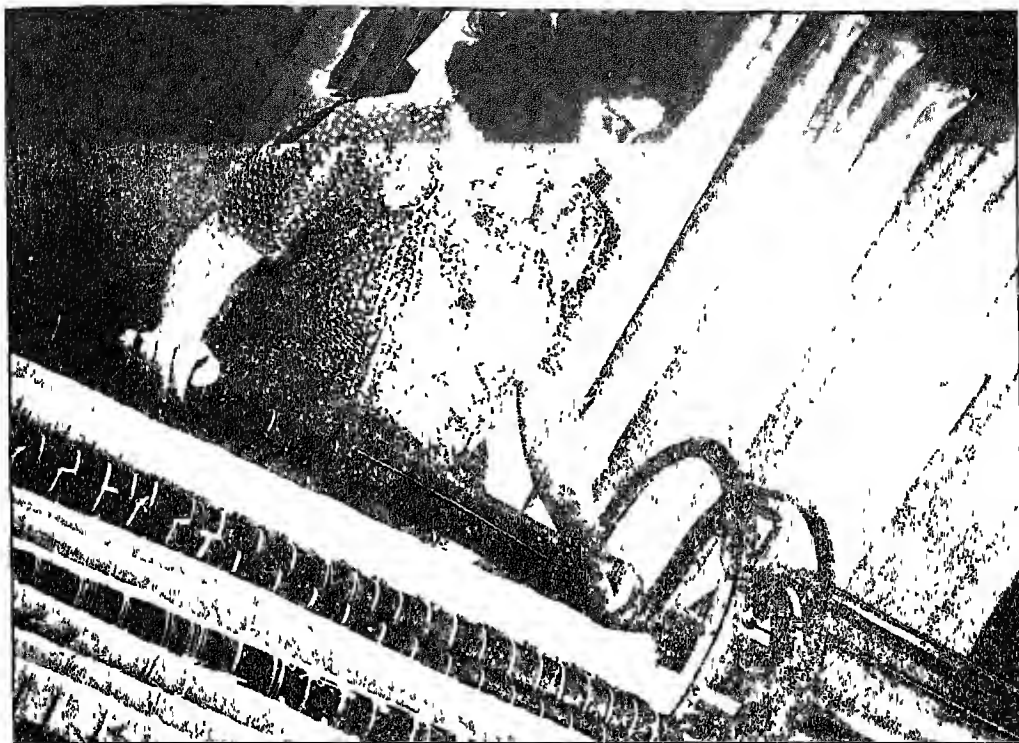
Another important variety of artificial silk is produced by treating cellulose with a mixture of acetic acid and acetic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$. The product is cellulose triacetate, $\text{C}_6\text{H}_7(\text{O})_2(\text{Ac})_3$. By partial hydrolysis this substance is converted into a mixture of



Courtesy of du Pont Company

Figure 287 Rayon Yarn

This type of rayon is called Cordura and is used to make the cord of tires



Courtesy of du Pont Company

Figure 288 Hanks of Nylon

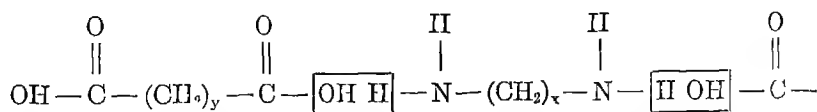
This form of Nylon is used to make the bristles of tooth and hair brushes

cellulose di- and triacetates. The mixture is dissolved in acetone, and the solution is forced through small holes into a chamber filled with warm air. The acetone quickly evaporates, leaving dry threads of cellulose acetate, which are then spun into larger, stronger threads to be used in making cloth.

8 Nylon

Of the new fabrics none, with the exception of Rayon and Celanese, has created more interest than Nylon, a product of the

du Pont laboratories. Diamines, consisting of two amine, NH_2 , groups connected by a chain of CH_2 groups, e.g., $(\text{NH}_2) - (\text{CH}_2)_x - \text{NH}_2$, react with dibasic organic acids also of the straight-chain type, e.g., $\text{HOOC} - (\text{CH}_2)_y - \text{COOH}$, to form compounds consisting of long molecules made up of alternate diamine and acid units. Molecules of water are removed, thus providing the bonds that link the nitrogen atom of one molecule to the carbon of a carboxyl group of the other molecule.



The different forms of Nylon depend upon the diamine and the acid used in this reaction. The product is similar to a protein in composition. After the Nylon has been

melted, it is forced through small openings, and thus the thread is made. When the threads have solidified, they are made into yarn, which is woven into cloth that re-



Courtesy of du Pont Company

Figure 289 New Uses for Nylon

These articles include paint brushes, parachute harness, parachute shroud lines, rope for gliders, parachute cloth, camouflaged parachute cloth, nylon rope, bearings, carburetor diaphragm, and surgical sutures

sembles silk both in composition and in properties. It is said to be more durable and more elastic than silk, wool, or cotton. Its first use was in making hosiery, but it is now used to make brush bristles, strings for tennis rackets, insulation for electrical wiring, and many other articles formerly made of natural silk.

SUBSTANCES RELATED TO MEDICINE

We can mention here only a few of the many substances of interest and value to the medical profession. Some of these are of natural origin, and some are produced synthetically.

9 Alkaloids

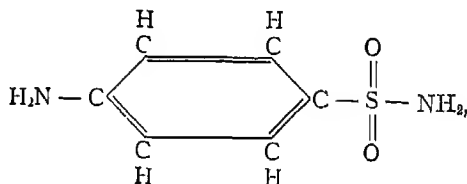
Alkaloids are basic nitrogenous substances obtained from plants. Most of them

are powerful drugs and many are very deadly poisons. The salts of alkaloids with sulfonic or hydrochloric acid are used in medicine instead of the pure alkaloids. Some of the most important alkaloids are listed in Table 35. Other alkaloids include caffeine from coffee and muscarine from toadstools.

During the recent war this country could not obtain quinine, which was badly needed for the treatment of malarial cases, from the Dutch Indies, the usual source of supply. Research developed an effective substitute called *atabrine*.

10 Sulfa Drugs

The medical profession has long been deeply interested in the discovery of drugs that can be used effectively and safely to combat the bacteria that produce diseases such as tuberculosis, typhoid, pneumonia, cholera, and others. About 1935, the organic compound, *sulfanilamide*,



was found to be an effective bactericidal agent especially when used against the streptococci responsible for the condition generally described as "blood poisoning." Since that time, many other closely related substances have been produced, and their effectiveness as bactericidal agents has been tested. Some of them have proved more effective than sulfanilamide itself. They are called, in general, the *sulfonamides* or, more commonly, the *sulfa drugs*. Some of the most widely used members of this group are *sulfopyridine*, which has been effective in the treatment of pneumonia, *sulfathiazole*, and *sulfadiazine*.

11. Antibiotics

Within the last few years, it has been found that certain micro-organisms produce sub-

TABLE 35

Some Important Alkaloids

Alkaloid	Source	Formula	Use
Quinine	Bark of Cinchona tree	$C_{20}H_{21}N_3O_2$	Treatment of malaria
Strychnine	Nux vomica	$C_{21}H_{22}N_2O_2$	Hair tonics
Morphine	Poppy	$C_{17}H_{19}NO_3$	Tonic, stimulant
Atropine	Belladonna	$C_{17}H_{23}NO_3$	Produces sleep
Nicotine	Tobacco	$C_{10}H_{11}N_2$	Dilates pupil of eye
Cocaine	Cocoa leaves	$C_{17}H_{21}NO_4$	Very poisonous, insecticide
Novocaine	Synthetic	$C_{13}H_{20}N_2O_2$	Local anesthetic

stances that destroy other micro-organisms, including certain kinds of disease-producing bacteria. The substances thus produced are called *antibiotics*. They are also effective in the treatment of the virus types of disease. The two best known antibiotics are *penicillin* and *streptomycin*. The former is obtained from a mold called *penicil-*

lum notatum. Streptomycin is produced by a micro-organism found in the soil and called *streptomyces griseus*. It is said that it offers great promise for use in treating cases of tuberculosis. It is also used in treating meningitis and tularemia. Penicillin is widely used in fighting many infectious diseases, especially pneumonia.



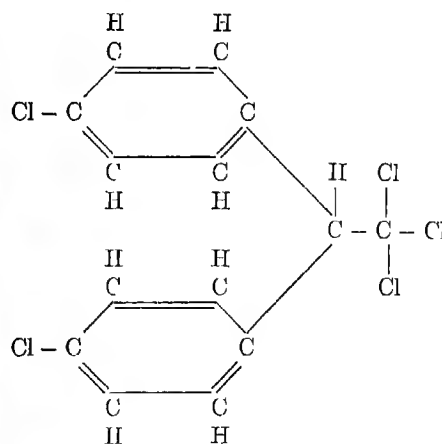
Courtesy of H. J. Inc.

Figure 290 Penicillin

Penicillin is another of the amazing new drugs used to combat infections. The droplets of liquid on this mold are rich in penicillin, which is extracted in tiny quantities after intricate separation and refinement processes.

12. A New Insecticide

A new insecticide, commonly known as DDT, has recently received much publicity. Its chemical name is *dichlorodiphenyltrichloroethane*, and its formula is



DDT has been found very effective in killing many insects that are instrumental in causing or carrying certain diseases. It kills, for example, the malarial mosquito, the louse that spreads typhus, and the common house fly. It is also used to kill moths.

roaches, and many other insects. It is especially useful because objects that have been treated with a spray composed of a solution containing it are protected against insects for long periods of time.

13. Hormones

Hormones are substances produced by the "ductless" glands of the body. These substances pass directly into the blood. Minute traces of the hormones affect biological processes profoundly. The exact number of these substances produced in the body is unknown. The more we learn about them, the better we may hope to combat many of the diseases which impair the normal functions of the organs of the body. Two of the hormones have been prepared in the laboratory: *thyroxine* ($C_{15}H_{11}O_4NI_4$) and *adrenalin* ($C_9H_7(OH)_2 - CHOH - CH_2 - NHCH_3$). *Thyroxine* is produced in the body by the thyroid gland. A lack of this substance causes goiter and cretinism, a disease resulting in deformity of the body and impairment of the functions of the brain. Although commonly regarded as a hormone, it is not so classified by every scientist of the biological chemical field. *Adrenalin* (epinephrine) is produced naturally by the adrenal glands. It acts as a stimulant of the heart and lungs. *Insulin* is also a hormone. It is produced in the pancreas and aids, in some way, in the metabolism of sugar. Some of the sex hormones have been produced synthetically. In all, some ten or twelve hormones have been identified.

PERFUMES

14. Composition and Production of Perfumes

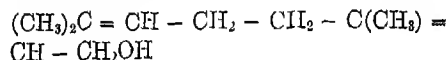
Some of the substances used in preparing perfumes are extracted from flowers, others are derived from materials obtained from animals, and some are prepared synthetically. The aromatic compounds of flowers are extracted either by the use of organic solvents, such as alcohol, or by distillation with steam. The finished perfume is likely to be a blend which often contains substances prepared synthetically. The aromatic substances are sold and used as alcoholic solutions. Attar of roses is prepared by the steam distillation of rose petals. From 30,000 to 50,000 roses are used to prepare an ounce of the oil,

which separates as a distinct layer from the water of the distillate. The principal ingredients of attar of roses are phenyl ethyl alcohol, $C_6H_5 - CH_2 - CH_2OH$, and geraniol, an unsaturated alcohol.

Phenyl ethyl alcohol can be produced in the laboratory and is often used to make rose water and the cheaper grades of rose perfumes.

Two of the most valued substances of the perfume industry are *musk* and *ambergris*. Musk is obtained from the musk ox, which lives in the Himalaya Mountains, and ambergris is a secretion which is found in the intestines of sperm whales. Synthetic musks are produced.

The perfumes of flowers and fruits belong to many classes of organic compounds. Oil of wintergreen, for example, is an ester of methyl alcohol and salicylic acid, and banana oil is amyl acetate, which is also an ester. Orange and lemon oils contain terpenes, which are aromatic hydrocarbons. Geraniums, citronella, attar of roses, and apples owe their fragrance in part to geraniol, an unsaturated alcohol.



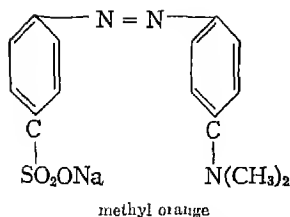
Other aromatic substances are ketones, phenols, and aldehydes.

The production of synthetic perfumes has required long periods of research, involving the determination of the composition of the natural substances, the determination of the structural formula of each component, and, finally, the blending of the synthetically prepared substances in the correct proportions to imitate the natural fragrance as closely as possible. The fruits of these extensive researches have sometimes improved upon nature, giving perfumes that cannot be found in any fruit or flower. And at the same time, many of nature's most highly valued odors have been successfully imitated. Among these are the fragrances of the rose, lily of the valley, heliotrope, narcissus, and violet. Similar successes have been attained in the production of synthetic flavors, such as vanilla.

DYES AND DYEING

15. Dyes

Until about the middle of the nineteenth century, dyes were obtained from natural



Crystal violet, eosin, fuchsin, and Bismarck brown are examples of dyes used in staining biological specimens for microscopical examinations. Several dyes, including gentian violet, methylene blue, and malachite green, are used as antiseptics.

16 Classification of Dyes

Dyes can be classified according to the methods used in applying them to materials. The classification that we give below is a very general one. The methods of application differ considerably, depending upon the chemical nature of both the dye and the material to be dyed.

Direct Dyes A direct dye is one that is attracted and held either in chemical combination or mechanically by the material to be dyed. Most of these dyes are acids or bases. The cloth to be dyed is immersed in a solution containing a salt of the dye. If the dye is an acid, this solution also contains acetic or dilute sulfuric acid to release the dye from its salt. If the dye is basic in nature, the solution contains a salt of the dye and a base. This method of dyeing is widely used in the coloring of silk and wool. Animal fibers appear to undergo hydrolysis in water, forming acid and basic substances which then may react with the dye.

Vat Dyes These dyes are not soluble in water. To apply them to cloth, they must first be converted into substances that are soluble. This change is, ordinarily, a reaction in which the dye is reduced to a "leuco" compound. The cloth is impregnated with a solution of this compound, usually in the presence of an alkali. The "leuco" compound is then oxidized to form the dye which, since it is not soluble, is precipitated

on and in the fibers of the cloth. Indigo is a vat dye.

Developed Dyes Some dyes are made, or developed, directly on the cloth. The cloth is first impregnated with one reactant and then treated with another substance which will react with the first to make the dye. The dye produced must, of course, be insoluble if a "fast" color is to be obtained.

Mordant Dyes To produce "fast" colors, many dyes must be used with a mordant. This is especially true when these dyes are used to color cotton or linen. The use of a mordant is illustrated by the following example in which aluminum hydroxide serves to hold the dyestuff in permanent combination upon cotton. The cloth is soaked in a solution of aluminum acetate, which readily hydrolyzes to form insoluble aluminum hydroxide. This reaction is favored by exposing the cloth, which has been soaked in a solution of the salt, to steam. The aluminum hydroxide is formed throughout the cloth and is held by the cotton threads and fibers. The cloth is now dipped into a bath containing the dye, which is adsorbed or chemically precipitated by the aluminum hydroxide. The attachment of the dye and the hydroxide is permanent and consequently the color of the cloth is made "fast." If the aluminum hydroxide is precipitated in a solution of the dye, it adsorbs the coloring matter and forms a highly colored precipitate, called a lake. The common mordants include the salts of aluminum and iron, tartar emetic, tannic acid, and potassium dichromate.

Review Exercises

1. To what kinds of compounds do the terms *polymer*, *high polymer* and *co-polymer* apply?
2. From what organic compounds are Buna S and neoprene produced?
3. Define, identify or explain the meaning of the following: butadiene, elastomer, isoprene, styrene.
4. What property do all those substances called plastics possess?

- 5 Distinguish between thermoplastics and thermosetting plastics
- 6 Enumerate some of the important groups of synthetic plastics and name the substances or kinds of substances used to make them
- 7 How do cotton and wool differ in composition?
- 8 Describe the process by which Rayon is produced. What is the chemical nature of Rayon?
- 9 What are cellulose triacetate, cellophane, keratin, atabrine, nicotine, quinine, and sulfanilamide?
- 10 What kinds of substances are used to produce Nylon? Why can it be said that Nylon more closely resembles natural silk, in composition, than does Rayon?
- 11 What is an antibiotic? Name two.
- 12 Many synthetic dyestuffs are sometimes classified as coal tar dyes. Why is this term appropriate?
- 13 Classify dyes according to the methods used in applying them to cloth.
- 14 The statement is sometimes made that limestone and coal are raw materials used in the production of at least one kind of synthetic rubber. Is this statement true? Explain.
- 15 In what way was petroleum related to the production of synthetic rubber during the recent war?

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ENERGY IN CHEMICAL CHANGE

Caloric (heat), on the supposition of it being material, is a subtle fluid, the particles of which repel one another, but are attracted by all other substances

TURNER, 1828

1. Introduction

Previously, we have discussed on several occasions the importance of energy in chemical reactions. In one of the early chapters, for example, we learned that no reaction occurs without the liberation or the absorption of energy in some form, usually as heat, and hence we have classified (page 151) reactions that liberate heat as exothermic and those that absorb heat as endothermic. Numerous examples of the effect of heat upon reacting systems and upon their states of equilibrium have been met in our studies of the production of ammonia, nitric acid, sulfuric acid, and other substances of commercial importance. Numerous illustrations of the use of electrical energy in the production of substances by electrolysis (page 110) or as a source of heat energy in the electric furnace (page 308) have also been described. We have studied, also, the liberation of energy from radioactive elements, either as gamma rays or as the kinetic energy possessed by swiftly moving beta and alpha particles. Everywhere, in fact, throughout our study of chemistry we have found energy occupying a position of importance, second only to that of matter.

So important is the subject of energy to the chemist that no treatment of the subject of chemistry can be considered complete without a chapter devoted to the energy of chemical change. This subject is particularly important in connection with the metals with which the closing chapters of

this book deal. Not only are electrical energy and heat energy extremely important in the production of the metals from their ores, but the metals themselves, or certain of their compounds, are depended upon to produce electrical energy in electrochemical cells and batteries. Let us first, however, consider the *heat energy* involved in chemical changes.

2 Energy Changes in Reactions

The energy absorbed or liberated during a chemical reaction represents the difference between the energy content of the reacting substances as compared with the energy content of the products of the reaction. Energy is released when the energy content of the products is smaller than that of the reacting substances. But if the reactants contain less energy than the products, the reaction can occur only when and if the additional energy is absorbed from the surroundings, or is supplied in some way from an outside source.

Sometimes our chief concern in a reaction is not what substances it may produce but the kind and quantity of energy that it liberates. In burning coal and wood as fuels, we are not interested in the carbon dioxide and water that are produced in the combustion, in fact, we do everything we can to facilitate their escape. We may have some interest in the ash, but only because it represents a portion of the fuel that we cannot use to liberate energy. We are concerned, pri-

manly, with the quantity of energy that can be released when a definite weight of the fuel is burned. So important is this question that we judge the value of a sample of coal largely by its *calorific value* (page 290). Likewise, we are interested, not in the products of the chemical changes that occur in a storage battery, or other types of electrochemical cells, but in the electrical energy output of these cells. In other cases, it is important that we know, or be able to determine, the energy that must be absorbed before the reaction can occur, for energy is expensive, as expensive as matter, and the amount of energy required to carry out a process must be as seriously considered as the cost of the raw materials used in the process. The study of the heat changes accompanying chemical reactions furnishes information about the reaction itself, and often gives valuable clues as to the exact nature of the changes that occur in the different parts of the reacting system.

The *heat of a reaction* is expressed as the number of calories liberated or absorbed in the production of the number of gram-molecular weights of the products indicated in the equation for the reaction. It is calculated for a constant temperature, that is, for a temperature of the products that is the same as the temperature of the initial state of the system.

3. Measuring the Heat of a Reaction

A *calorimeter* is used to measure the heat absorbed or liberated by chemical reactions. This instrument consists essentially of a vessel in which the reaction is carried out, and which is carefully insulated to prevent heat exchanges with the surroundings. The vessel may be a glass flask with double walls, the space between the walls is evacuated to provide insulation. The cover is made of some substance that also acts as an insulator. It is perforated to take an accurate thermometer, a tube through which the reactants can be added, and a stirrer. A simple calorimeter for elementary experi-

ments can be constructed by placing a beaker upon corks within a larger beaker and providing an insulating cover.

To determine the heat of the reaction between a solution of sodium hydroxide and hydrochloric acid, for example, measured volumes of the two solutions, which must be of known concentrations, are poured through the tube into the inside vessel of the calorimeter. The temperature of the two solutions should be known, and for convenience they should be the same, before they are mixed in the calorimeter. The stirrer is started and the maximum temperature reached by the reacting mixture is noted. The rise in temperature is multiplied by the heat capacity of the solution and the heat capacity of the calorimeter (expressed in calories per degree of temperature) to determine the heat of the reaction in terms of the number of calories liberated.

4. The Bomb Calorimeter

In the bomb type of calorimeter, which is used in determining the calorific value of fuels, a bomb made of strong steel is used as the inside vessel. The bomb is lined with an alloy that is resistant to chemical action, and it is fitted with a tight screw-cap cover. The sample whose calorific value is to be determined is placed in a small platinum cup (Figure 291), and a small iron wire is embedded in the charge. The wire is connected to the terminals of the electrical circuit on the cover of the bomb. Oxygen, under pressure, is forced into the bomb through a valve at the top, and the bomb is then completely immersed in a definite quantity of water in a well insulated outer vessel. A thermometer for the measurement of temperature changes and a stirrer are suspended in the outer vessel. The electrical circuit is then closed, whereupon the iron wire becomes hot enough to ignite the sample. Combustion proceeds rapidly in the presence of the compressed oxygen, and the heat is absorbed largely by the water, which consequently undergoes a rise in temperature. Some of the heat is also used to raise the temperature of the bomb, the stirrer, the walls of the outside vessel, and other parts of the apparatus to the same temperature that the water attains. The quantity of

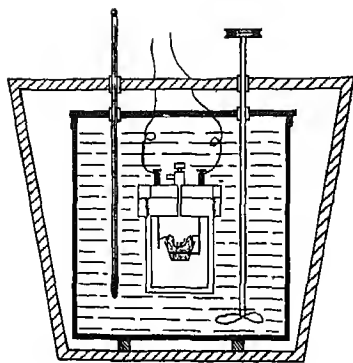


Figure 291 A Calorimeter

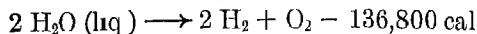
heat liberated by the combustion is calculated upon the basis that one calorie raises the temperature of one gram of water one degree Centigrade. From the specific heats and weights of the materials in the apparatus, a correction is made for the heat which they absorb. This is added to the heat absorbed by the water in finding the total heat of the reaction.

In expressing the caloric value of fuels, and sometimes in industrial practice involving other reactions, the British thermal unit (B.T.U.) is used as the unit of heat, instead of the calorie. This unit represents the quantity of heat which is required to raise the temperature of one pound of water one degree Fahrenheit. This quantity of heat is equal to 252 calories.

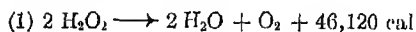
5 Thermochemical Equations

Since energy changes always accompany chemical reactions, the quantity of energy involved is as important a part of a chemical equation as the number of molecules of the reactants. In many reactions the energy changes are of no great concern to the chemist, and the number of calories liberated or absorbed is not indicated. In other cases, however, the energy may be of as much importance as the weights of the reacting substances, and for such reactions *thermochemical* equations are written. If there can be any doubt concerning the physical states of the reacting substances and the products, these states should be indicated in the equation. More energy is required to decompose a definite weight of liquid water,

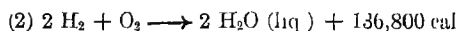
for example, than is required to decompose the same weight of water which has already been converted into the gaseous state. The decomposition of liquid water is shown, therefore, by the following equation



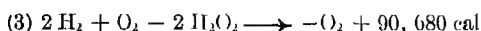
Throughout our discussion of the chemistry of the elements and their compounds, we have found many reasons to write equations of this kind. There is nothing that we need to add about them at this time, except to say that thermochemical equations may be added and subtracted to calculate the heats of reactions that have not been studied, or to find the heats of formations (from their elements) of compounds that are not formed by the direct combination of the elements. As an illustration of such calculations, let us take the determination of the heat of formation of hydrogen peroxide from hydrogen and oxygen. The direct synthesis of this compound from the two elements is not possible, but we may calculate the heat of this reaction as follows. We know the quantity of heat liberated when two gram-molecular weights of hydrogen peroxide (in dilute solution) decompose



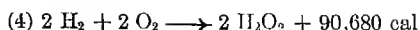
We also know the heat of formation of water, when this substance is synthesized from the elements



We may now write the following equation in which the water is eliminated by subtracting (1) from (2)



This equation may also be written in the following form



The heat of formation of hydrogen peroxide (in dilute solution) is shown to be 45,340 calories per gram-molecular weight

6 The Free Energy of Substances and the Free Energy Changes of Reactions

Every substance is a storehouse of energy, and the quantity of energy that each substance possesses per unit of mass is definite at a definite temperature. This energy appears to be intimately related to the chemical properties of the substance. In considering chemical reactions, however, it is not the energies of the reacting substances that are important, it is the change in energy that accompanies the change of the reacting substances into the products of the reaction. For every reaction—that occurs without being forced to do so by energy from an outside source—there appears to be a driving force that determines the tendency of the substances to react. For some substances this driving force is strong, for others it is weak. Thus, there is evidently a strong driving force that determines the tendency of hydrogen and chlorine to combine, of trinitrotoluene to decompose, and of sodium to react with water. There is a weaker force causing carbon to combine with oxygen, iron to rust, and hydrogen to combine with nitrogen to form ammonia. For some reactions there appears to be no driving force at all, such reactions, therefore, do not occur spontaneously. For a given reaction the driving force determines the equilibrium constant of that reaction. If the driving force is strong, the reaction will be more nearly completed, and the equilibrium constant will be larger than if the driving force is smaller. If the driving force is very weak, the equilibrium constant will be almost zero.

This same driving force is also a measure of the amount of work that the reaction can be made to do, the greater the driving force, the greater is the amount of work. We understand, of course, that a reaction for which the driving force is strong will occur whether the work is performed or not, if no work is done, the energy that might have been used to perform work is converted into heat. Let us consider the reaction between a strip of zinc and the cupric ions in a solu-

tion of cupric sulfate. If the zinc is immersed in the solution, it dissolves and cupric ions are changed into metallic copper. No useful work is done by the reaction that is carried out under these conditions, but the driving force of the reaction has been utilized, and the capacity of the system to react has been decreased. Now if the zinc is placed in one beaker along with a solution of zinc sulfate, and the solution of cupric sulfate is placed in a second beaker, the same reaction as before can be made to occur but the reactants will not be in contact directly. To complete the arrangements that are necessary for the reaction a copper wire is dipped into the solution of cupric sulfate, and the other end is connected to the strip of zinc. The two solutions are connected with an inverted U tube filled with a solution of sodium chloride, this tube is necessary to complete the electrical connections between the two electrodes, copper and zinc. As the zinc dissolves at one electrode and copper is deposited at the other, a current of electricity flows through the wire, this current represents electrical energy that can be made to do work.

It appears, therefore, that the most satisfactory measure of the driving force of a reaction is the work that can be obtained from the reaction, or better still, *the energy that is liberated by the reaction at constant temperature and pressure, and that can be converted into work if suitable mechanisms for its utilization are provided*. This energy is the *free energy change* of the reaction. We assume that the substances at the beginning of the reaction possess definite quantities of free energy, as do the substances produced by the reaction. We have no means, however, of measuring these quantities, the absolute free energies of different substances. *All that we can measure is the change in free energy of the entire system as the reaction occurs*.

The chemist is interested in free energy changes because this information helps him to determine the possibilities of a chemical reaction, how nearly complete it will be,

how much product he can prepare from a given amount of the starting materials, and so on

For some reactions, the free energy change is approximately the same as the heat of the reaction (Table 36). In the reactions leading to the formation of some compounds, the free energy change is greater than the heat liberated. If this is the case, the difference must be absorbed from the surroundings, which consequently become colder. If the heat of the reaction corresponds to a larger amount of energy than the free energy change, a certain amount of heat will be given up to the surroundings. This heat, of course, cannot be used to perform work. All information of this kind is of value to the chemist in determining just what may be expected of a given reaction, most important of all, it tells him whether or not a given reaction can be used for his purposes.

TABLE 36

Free Energy Changes and Heats of Formation *

Compound	Free Energy Change (gram calories per gram-molecular weight at 25°)	Heat of Formation
Ammonia (gas)	+ 3,910	+ 10,950
Carbon dioxide (gas)	+ 94,260	+ 94,400
Carbon monoxide (gas)	+ 32,510	+ 26,400
Hydrogen sulfide (gas)	+ 7,840	+ 5,260
Nitric oxide (gas)	- 20,850	- 21,500
Water (vapor)	+ 54,507	+ 57,800

* The reactions involve the formation of the compounds from their elements. A negative value indicates that energy is absorbed during the reaction.

7 Energy of Activation

Both the change in free energy and the heat of the reaction by which water is produced from its elements are relatively large. Why, then, do hydrogen and oxygen not combine readily and immediately at ordinary temperature? We touched upon this subject lightly on page 419. Before hydrogen and oxygen can react, their molecules must be broken up, that is, the bonds uniting the atoms of the diatomic molecules, H_2

and O_2 , must be broken. When these changes have occurred, the atoms may then combine to form molecules of water in which atoms of hydrogen and atoms of oxygen share electrons. In the beginning, under ordinary conditions, there is no energy available to sever the bonds between atoms of the free elements. When the reaction once starts, the energy released when atoms of hydrogen and oxygen combine will be sufficient to break the bonds between atoms of H_2 and O_2 — and more, too, because some is left over to appear as heat. To start the reaction, additional energy must be given to the atoms or molecules so that they may be changed into the state that is necessary, if they are to form molecules of water. This additional energy is called the *activation energy* of the reactants. Substances may be activated — the additional energy required may be supplied — by an increase in temperature which results in collisions that are more effective in breaking bonds. The addition of energy may also make valence electrons more readily available for transfers to other atoms or for forming shared electron pairs with other atoms, because, when energy is absorbed, then electrons are displaced from their normal energy levels and shifted to higher levels where they are farther removed from the nucleus and where, consequently, they are less completely under the influence of the nucleus of their parent atom. Thus, in some instances, heat may completely remove one or more electrons from an atom, thus producing a positive ion. Energy of activation may also be supplied by radiations, such as light or X-rays, or it may be supplied by bombarding atoms and molecules of the reactants with rapidly moving alpha and beta particles or other sub-molecular bits of matter. Naturally, the energy of activation differs for different substances.

ELECTROCHEMICAL CELLS

8. Electrical Units

We have described the passage of electricity through a conductor as a condition produced by

the flow of electrons (page 110). There is a certain degree of *resistance* that each conductor offers to this flow of electrons. The unit of resistance is the *ohm*, which is defined as the resistance (at 0°) of a column of mercury 106 300 cm long and weighing 14 4521 g. Electrons move through a conductor from a region of high electrical potential to one of lower potential at a rate proportional to the difference in potential. The difference of potential is also called the *electromotive force*. The unit of difference of potential is the *volt*, which is defined as the difference of potential required to cause a current of one ampere to pass through a conductor whose resistance is one ohm. The *ampere* is the unit of the current's strength. A current of one ampere will deposit 0.0011180 g, or 0.00001036 gram-atomic weight, of silver per second in the electrolysis of a solution containing silver ions. The *quantity of electricity* that flows through a conductor is equal to the product of the current strength by the time in seconds. The unit of quantity is the *coulomb*.

$$\text{Coulombs} = \text{Amperes} \times \text{Seconds}$$

The current strength, difference of potential, and resistance are related as follows:

$$C \text{ (in amperes)} = \frac{E \text{ (in volts)}}{R \text{ (in ohms)}}$$

The *quantity of energy* associated with the passage of electricity through a conductor depends upon the quantity of electricity and the voltage (intensity). The unit of *electrical energy* is the *joule*, which is defined as the product of one coulomb by one volt.

$$\text{Joules} = \text{Coulombs} \times \text{Volts}$$

Electrical power refers to the rate at which electrical energy is made available and used. The unit of power is the *watt*, which is defined as one joule per second or one volt-ampere.

$$\text{Watts} = \text{Amperes} \times \text{Volts}$$

(One *horse-power* is equivalent to 746 watts. The *kilowatt* is 1000 watts, and the *kilowatt-hour* is one kilowatt for one hour, or 3,600,000 joules.)

9 Measuring the Free Energy Changes of Reactions

The most reliable method of determining the free energy change of a reaction depends

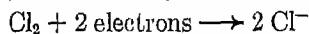
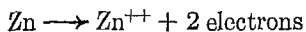
upon the measurement of the electromotive force (voltage) which is produced in an electrochemical cell or battery in which the reaction is carried out. For electrical energy, the electromotive force is a measure of the intensity and therefore of the availability of the energy for the performance of work, just as temperature is the intensity factor for thermal energy. The electromotive force which can be produced by means of a reaction, at a given temperature, is directly proportional to the free energy change of the reaction at that temperature. If the conversion of the free energy change of the reaction into electrical energy is complete:

$$\text{Free energy change} = \text{electrical energy} = \text{volts} \times \text{coulombs}$$

Many oxidation-reduction reactions that liberate energy and that proceed by themselves — spontaneously — can be used to produce an electric current, *provided it is possible for the reaction to occur when the substances are not directly in contact*. Oxidation must occur at one electrode, and reduction at the other, so that electrons will flow through a wire connecting the two. Some reactions cannot be used in this manner to produce a current, the oxidation of carbon by oxygen, for example, occurs only when the two substances are directly in contact with each other.

10. Production of Electrical Energy by Means of Oxidation-Reduction Reactions

Let us consider the simplest possible kind of an oxidation-reduction reaction, the direct combination of two elements. For the two elements, let us select chlorine and zinc. When metallic zinc is placed in a vessel filled with chlorine or is immersed in water saturated with chlorine, zinc is oxidized and chlorine is reduced. This reaction involves a transfer of two electrons from a zinc atom to two chlorine atoms, each chlorine atom accepting one electron.



Now the free energy change of this reaction is positive; therefore, the reaction occurs spontaneously. If it is carried out as we have described — that is, if the zinc and chlorine are in contact with each other — the total free energy change, which represents the maximum work that the reaction can do, is converted into heat, which is absorbed by the solution, the container, and eventually by the surroundings of the container.

Strange as it may seem, the reaction between zinc and chlorine can be carried out under conditions so that the two elements are not in contact with each other. Only under these conditions is it possible to convert any of the energy, which is otherwise liberated as heat, into a useful form such as electricity. To show how the reaction between zinc and chlorine occurs when these elements are not in contact, let us place a solution of some inactive electrolyte in each of two beakers. Sodium chloride serves this purpose very well since it reacts with neither zinc nor chlorine and at the same time forms a solution of excellent conducting properties. A small glass tube bent into the form of the letter U, is also filled with the salt solution and is used as a conducting bridge (Figure 292) between the solutions in the two beakers. Into one of the solutions we now place a graphite electrode, and the solution itself is saturated with chlorine. A graphite electrode is selected because it is not acted upon by chlorine. We place a zinc rod or strip in the other solution, and connect this by means of a wire (copper) to the graphite

electrode. We now have a simple *electrochemical cell*, which may be used as a source of an electrical current. At the surface of the zinc, atoms of this element pass into the solution as zinc ions (Zn^{++}), leaving two electrons, per atom, upon this electrode. The zinc becomes, therefore, the negative pole of the cell. At the graphite electrode, chlorine molecules are converted into chloride ions by removing two electrons, per molecule, from this electrode, which consequently becomes positively charged. Now electrons will flow out of the zinc through the wire and into the graphite, where they are, in turn, removed by the formation of the chloride ions from free chlorine. The flow of electrons through the wire connecting the zinc and the graphite constitutes an electrical current, which can be made to do useful work. When carried out in this manner, much less heat is liberated by the reaction as can be shown by observing the temperature attained in the solution, if, of course, some of the free energy is converted into electrical energy, there is less to appear as heat.

The electrons flow or move, of course, from the negative pole — where there is a greater concentration of them — to the positive pole — where there are fewer. According to an old convention, originating long before electrons were known, the current was assumed to flow from the positive to the negative pole. This convention is still sometimes used.

The function of the electrolyte in the cell described above, is to complete the electrical circuit

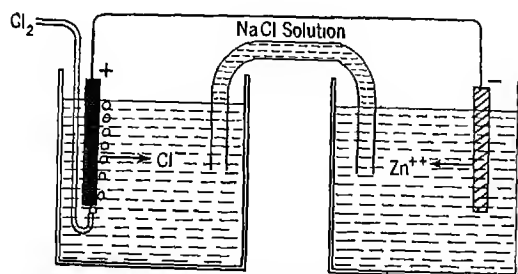


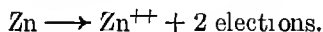
Figure 292 An Electrochemical Cell Based upon the Reaction $\text{Zn} + \text{Cl}_2 \rightarrow \text{Zn}^{++} + 2 \text{Cl}^-$

by making the liquid medium between the two poles of the cell a conductor. The tube serves as a conducting bridge by allowing the ions to migrate through the solution, the chloride ions migrate toward the graphite (positive) electrode, and the sodium ions migrate toward the zinc (negative) electrode. At the same time the tube prevents the chlorine and the zinc from coming in contact and reacting directly, as they would if both were placed in the same beaker.

Other types of oxidation-reduction reactions can be used in similar cells to produce electrical energy. We might use chlorine in one half of the cell and a solution of ferrous sulfate (FeSO_4) in the other, with small pieces of platinum foil serving as the electrodes. This reaction involves the conversion of ferrous ion (Fe^{++}) into ferric ion (Fe^{+++}), each ferrous ion giving up one electron to the electrode with which its solution is in contact. At the other electrode chlorine molecules are changed into chloride ions as before.

11. Equilibrium Between a Metal and a Solution of Its Ions

Let us consider a strip of zinc in contact with a solution containing zinc ions. Two opposing reactions are now possible. The atoms of zinc may pass from the strip of metal into the solution as zinc ions



The zinc ions which are already in the solution may remove electrons from the strip of metal and be converted into neutral atoms



The first of these reactions depends upon a characteristic property of zinc — upon the ease with which the atom will liberate two electrons. Every metal has a characteristic tendency to pass into the ionic state by losing electrons, this tendency is sometimes called the solution pressure of the metal.

For each Zn^{++} ion produced, two electrons are left on the strip of metallic zinc. A difference of potential between the metal and

the solution is thus produced and the metal, as a result of the electrons that accumulate on it, has a negative charge with respect to the solution.

The second reaction — the conversion of ions into neutral atoms of the metal — causes electrons to be removed from the metals. Here again, a difference of potential between the metal and the solution results, but in this case the metal has a positive charge with respect to the solution. The discharge of the ions occurs at a rate that depends upon the number of zinc ions that come into contact with the surface of the metal. Let us speak of this reaction as the *ion-discharging* tendency, it is referred to, also, as the osmotic pressure. Depending as it does upon collisions of ions with the metal, this tendency will vary with the rate at which the ions move, and therefore will be different for different temperatures. It will also vary, at a given temperature, with the concentration of the ions, being strongest when the concentration is greatest. *The rate at which the ions are discharged depends, also, upon the electrostatic force of attraction between the positive ions and the metal, which has a negative charge as a result of the first reaction.* This condition gives rise to a difference of potential, or electromotive force (e m f) between the metal and the solution, and under the influence of this difference of potential, the positive ions will move toward the metal, at a rate which is greatest when the e m f has its maximum value.

If a metal is placed in contact with a solution of its ions, either the solution pressure or the tendency of the ions to precipitate may be the greater. The actual result will depend upon the metal used and the concentration of ions in the solution. Let us consider the two possibilities.

(1) If the metal is at least fairly active, and if the concentration of the metal's ions is not extremely great, the solution pressure of the metal will be the stronger of the two tendencies. Under these conditions, the metal will pass into the solution as ions

(reaction 1), leaving electrons on the undissolved metal. For active and moderately active metals the solution pressure overbalances the effect of any concentration of the metals' ions that can be obtained.

(2) If, however, the concentration of the ions of the metal is sufficiently great, and especially if the metal is not very active, it may happen that the rate of discharge and deposition of the ions upon the surface of the metal will be greater than the rate of formation of ions from the metal. In this event, the ions will be deposited, giving a *positive charge to the metal* and setting up an e m f between the metal and the solution.

It will be noted that both possibilities that we have just described result in an e m f that opposes the very reaction that produces the e m f. Under the first conditions — when solution pressure is the stronger — the e m f is produced as the ions of the metal pass into the solution, leaving a negative charge upon the metal. This charge, however, causes the positive ions of the metal to be attracted back toward the metal, and therefore increases the tendency of the ions to be discharged. But if the electrolytic solution pressure represents the weaker tendency, then the e m f depends upon the production of a *positive* charge upon the metal, and as this charge grows larger, it causes the ions to be attracted less strongly toward the metal.

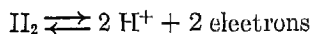
It is evident, therefore, that the e m f produced between the metal and the solution depends upon the difference between (1) the tendency of the ions to form as a result of the metal's solution pressure and (2) the tendency of the ions to deposit as determined by their concentration. By measuring the electromotive force, or difference of potential, that results when each of a series of metals is placed in contact with a solution of its ions, we may determine the relative order of magnitude of the electrolytic solution tension of the different metals. In order that this comparison can be made, the concentrations must be comparable, or more strictly speaking, the activities (page 442) of the ions of the different metals must be the same.

12 The Hydrogen Electrode

The measurement of the potential difference between a metal and a solution of its ions is not so simple as it may appear. This potential cannot be measured, for example, by connecting one end of a voltmeter with the metal and the other with the solution.

In practice, the metal and a solution of its ions (of known concentration) is used as one half of an electrochemical cell, and an electrode of constant potential difference — a standard electrode — is used as the other half of the cell. The *hydrogen electrode* can be used for this purpose.

This electrode consists of a small platinum foil coated with black, spongy platinum. The metallic foil is placed in a solution containing hydrogen ion (at unit activity), and pure hydrogen is bubbled into the solution under a pressure of one atmosphere. The platinum adsorbs hydrogen, which establishes equilibrium with the hydrogen ions in the solution:



The platinum and its adsorbed hydrogen act, therefore, as an electrode of hydrogen, and a potential difference is set up between the solution and this electrode.

13 Measurement of Electrode Potentials

The electrode potential of a metal, such as zinc, is the potential produced when the

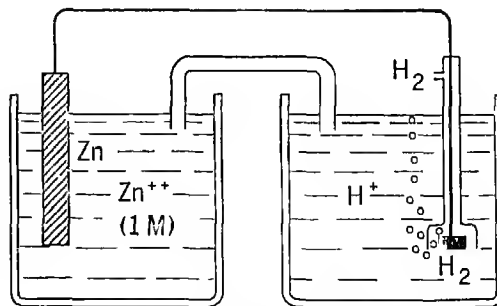


Figure 293 The Measurement of Electrode Potentials

This cell explains the theoretical basis of the method; in practice, electrodes other than the hydrogen electrode are usually employed, but their potentials are expressed in terms of the hydrogen potential.

metal is immersed in a solution containing a definite concentration of the ions of the metal. To measure the electrode potential of a metal an electrochemical cell is set up, consisting of the metal and a solution of its ions as one half of the cell and a hydrogen electrode (or some other standard electrode) as the other half (Figure 293). The two halves of the cell are connected by a curved glass tube filled with a solution of potassium chloride, or some other electrolyte, and also by a wire that connects the metal with the platinum foil of the hydrogen electrode. The potential difference of the cell as a whole can now be measured.

The result of this measurement consists of the combined effects of the potential difference between the metal and the solution in which it is immersed, the potential difference between five hydrogen and hydrogen ions, and the potential difference between the solutions, themselves. Of the factors composing the total electromotive force of the cell, the potential of the hydrogen electrode may be kept constant in the study of the potentials of different metals, the potential difference between the two solutions is made small by using the connecting tube filled with a solution of potassium chloride, and, since this KCl-bridge is used in all the cells, the potential between the solutions may be disregarded without introducing serious errors. The potential of the hydrogen electrode is usually defined arbitrarily as zero for the sake of convenience. When this is done, *the entire electromotive force of the cell may be regarded as the difference of potential between the metal and its solution.* The measured potential of this electrode is, consequently, not the real potential, which would be equal to the observed potential corrected for the potential of the hydrogen electrode. However, the latter is constant for the potential measurements of a series of metals, and when these potentials are to be compared, this correction need not be made. The e.m.f. values obtained by such measurements are called the electrode potentials of the metals.

Instead of the hydrogen electrode, one half of the cell may consist of a *calomel*, Hg_2Cl_2 , electrode. Metallic mercury is placed in a solution of 1 N potassium chloride, the solution is saturated with mercurous chloride, and an excess of solid mercurous chloride, or calomel, is added. As measured against the hydrogen electrode, the potential of the calomel electrode is + 0.28 volt.

14. The Electrochemical Series

Measurements of the electrode potentials of different metals made in the manner described in the preceding section may be used to determine the relative positions of these metals in the electrochemical series. When used as electrodes in one half of the cell, some metals will dissolve, forming positive ions. The formation of the ions leaves electrons upon the metal, which consequently acquires a negative charge. If the metal is connected by a conductor (external to the solution) with the hydrogen electrode, these electrons will flow from the metal to the hydrogen electrode, where they are used to convert hydrogen ions into neutral atoms of hydrogen. This condition results whenever the metal has a greater tendency to form positive ions (by losing electrons) than hydrogen has. The electromotive force of such a cell, in which zinc (and Zn^{++} ions at unit activity) is used as the metal, is 0.76 volt. This is called the electrode potential of zinc. It is given a *negative* sign (page 634), since zinc is the negative pole of the cell. When other metals are used, the electromotive force of the cell will have different values, depending upon the relative tendency of the metal (as compared with hydrogen) to give up positive ions to the solution. Lead, for example, gives an electromotive force of only 0.12 volt, because its atoms have a weaker tendency than zinc atoms to become positive ions. Or, to put the matter in another way, there is only a slight difference between lead and hydrogen in their tendencies to change into positive ions. It is clear, therefore, that if we measure the electromotive force of cells in which different metals

are used, the results will give us the order of these metals in the electrochemical series, in which the relative position of a metal depends upon the ease with which its atoms lose electrons and become positive ions.

When we replace zinc or lead with copper, we find that hydrogen has a stronger tendency to form positive ions than the metal. Hence, if we connect a normal hydrogen electrode to a strip of copper immersed in a solution of a cupric salt in which the activity of the cupric ions is unity, cupric ions are changed into neutral atoms, and the copper becomes the *positive* pole of the cell. At the hydrogen electrode, hydrogen molecules are changed into hydrogen ions, thus giving this electrode a negative charge. The electromotive force of this cell is 0.34 volt, which is

the electrode potential of copper. We give it a *positive* sign (Table 37), because copper is the positive pole of the cell in which the measurement is made. Copper becomes positively charged with respect to the normal hydrogen electrode.

If the non-metallic elements are included in the electrochemical series we find that they possess relatively high *positive* potentials. This condition depends upon the fact that the non-metals produce negative ions when they go into solution, and the neutral elements—the electrode—are left with a positive charge.

The table of potentials (Table 37) contains the electrode potentials of some of the non-metals as well as both active and inactive metals. The positions of the elements

TABLE 37
Electrode Potentials *

Element	Ion	Reaction at the Electrode	Potential (volts)
Potassium	K^+	$K \rightleftharpoons K^+$	-2.92
Calcium	Ca^{++}	$Ca \rightleftharpoons Ca^{++}$	-2.76
Sodium	Na^+	$Na \rightleftharpoons Na^+$	-2.71
Magnesium	Mg^{++}	$Mg \rightleftharpoons Mg^{++}$	-1.86
Aluminum	Al^{+++}	$Al \rightleftharpoons Al^{+++}$	-1.70
Manganese	Mn^{++}	$Mn \rightleftharpoons Mn^{++}$	-1.1
Zinc	Zn^{++}	$Zn \rightleftharpoons Zn^{++}$	-0.76
Sulfur (at Pt electrode)	$S=$	$S \rightleftharpoons S=$	-0.55
Iron	Fe^{++}	$Fe \rightleftharpoons Fe^{++}$	-0.44
Cadmium	Cd^{++}	$Cd \rightleftharpoons Cd^{++}$	-0.40
Cobalt	Co^{++}	$Co \rightleftharpoons Co^{++}$	-0.28
Nickel	Ni^{++}	$Ni \rightleftharpoons Ni^{++}$	-0.23
Tin	Sn^{++}	$Sn \rightleftharpoons Sn^{++}$	-0.14
Lead	Pb^{++}	$Pb \rightleftharpoons Pb^{++}$	-0.12
Hydrogen	H^+ (or H_3O^+)	$H_2 \rightleftharpoons 2 H^+$	0.00
Copper	Cu^{++}	$Cu \rightleftharpoons Cu^{++}$	+0.34
Silver	Ag^+	$Ag \rightleftharpoons Ag^+$	+0.80
Mercury	Hg^{++}	$Hg \rightleftharpoons Hg^{++}$	+0.80
Iodine	I^-	$2 I^- \rightleftharpoons I_2$	+0.53
Bromine (at Pt electrode)	Br^-	$2 Br^- \rightleftharpoons Br_2$	+1.07
Chlorine (at Pt electrode)	Cl^-	$2 Cl^- \rightleftharpoons Cl_2$	+1.36
Gold	Au^{+++}	$Au \rightleftharpoons Au^{+++}$	+1.36
Fluorine	F^-	$2 F^- \rightleftharpoons F_2$	+2.85

* The electrode potentials which are given in this table are based upon comparisons with the normal hydrogen electrode, which is arbitrarily taken as having a potential of 0.00 volts. The temperature is 25° C., and the pressure of the hydrogen is one atmosphere.

The concentrations of the ions in the different solutions are 1 molar or, as more accurately expressed, the values as given are for an *activity* (page 442) of unity. The higher a metal stands in this list, the more easily oxidized are its atoms and the harder to reduce to the free element are its ions. The non-metals lowest in the list are the best oxidizing agents. Their ions are the most difficult to oxidize to their free or uncombined state.

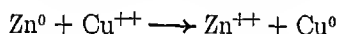
in this table represent the relative ease with which the elements can be oxidized by losing electrons. Those at the top are most easily oxidized. Conversely, the free non-metals and the metallic ions at the bottom are most easily reduced and serve, therefore, as the best oxidizing agents. This property results from the tendency of the atoms of these elements to attract electrons very strongly and to a very slight tendency on their part to give up any of the electrons that they possess or which they have acquired in chemical reactions from other elements.

The positive sign of the lower values in this table indicates that these electrodes would act as the positive poles of cells made up of these electrodes and the normal hydrogen electrode.

TYPES OF ELECTROCHEMICAL CELLS

15 The Daniell Cell

In the Daniell cell electrical energy is made available by means of the reaction between metallic zinc and cupric ions:



The construction of the cell is shown in Figure 294. The electrodes are made of metallic zinc and copper. Each electrode is placed in a solution of the ion corresponding to the metal, and the solutions are connected by means of a siphon U tube. If solutions containing metallic ions at unit activity are used, the potential difference between copper and the solution of cupric ions will amount to 0.34 volt and will be so directed that the copper electrode is posi-

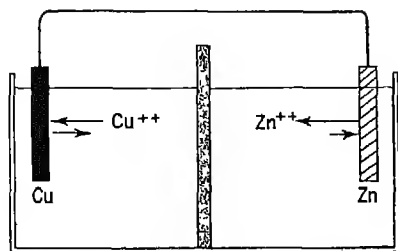


Figure 294 The Daniell Cell

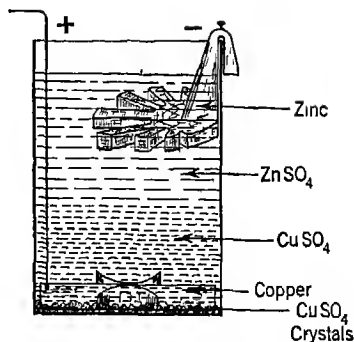


Figure 295 The Gravity Cell

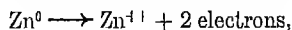
tively charged toward the solution. The difference of potential between zinc and a solution containing Zn^{++} ions at unit activity is 0.76 volt, and the zinc electrode is negatively charged (Table 37) as compared with the solution. If a wire is used to connect the two metals (outside the solution), an external circuit is made, and electrons flow from the zinc toward the copper. The differences of potential produced at the two electrodes act in the same direction, namely, to cause electrons in the external circuit to flow toward copper. For this reason the electromotive force of the cell is equal to the sum of the two electrode potentials:

$$0.34 + 0.76 = 1.10 \text{ volts}$$

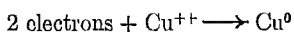
This is the theoretical voltage of the Daniell cell in which solutions containing Zn^{++} and Cu^{++} ions at unit activity are used. If solutions containing different ionic concentrations are used, the voltage will vary. The voltage of the cell may be increased by using more dilute solutions of zinc ion and more concentrated solutions of cupric ion. Can you show why these changes in concentration should favor the production of a higher e.m.f.?

The gravity cell makes use of the same reaction as the Daniell cell. The copper electrode consists of three sheets of copper which are fastened together and placed on the bottom of the cell. The metallic copper is placed in a saturated solution of cupric sulfate. To keep the solution saturated, crystals of cupric sulfate are placed in the bottom

of the vessel. To provide more surface a blanchet (crowfoot) zinc electrode is used. This is suspended near the top of the cell in a dilute solution of zinc sulfate, which floats on the heavier solution of cupric sulfate. When the two metals are connected externally by means of a wire, electrons flow through the wire from zinc to copper, since zinc becomes negatively charged by the reaction



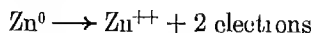
while copper is positively charged by the discharge of cupric ions



These reactions maintain the condition required for the flow of electrons through the external circuit. At first the voltage is comparatively high, but it falls off slowly as the zinc passes into solution, since the concentration of the zinc ions in the solution surrounding the zinc electrode gradually increases. As the concentration of the zinc ion increases, the zinc electrode becomes less negative, and the electrode potential decreases (page 635).

16 Concentration Cells

We have seen that the difference of potential between a metal and a solution containing the ions of the metal depends, at a given temperature, upon the concentration of the ions. It is possible, therefore, to construct a cell by using two electrodes of the same metal, if one electrode is placed in a concentrated and the other in a dilute solution of the ions of the metal. Strips of zinc may be used as the electrodes, and these may be placed in two solutions containing different concentrations of zinc sulfate. The same chemical reaction occurs at the two electrodes

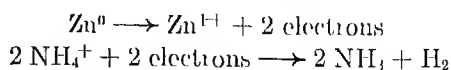


Since the electrode potential depends upon the concentration of zinc ions in the solution around the electrode, the electrode in the more dilute solution becomes more strongly negative toward the solution than the other. If the two zinc electrodes are connected externally, by a wire, the electrode in the more dilute solution will be negative toward the electrode in the more concentrated solution,

and electrons will flow from the former to the latter. As the electrons flow away from the negative zinc electrode, atoms of zinc will leave this electrode and pass into the solution as zinc ions, thus re-establishing the negative condition. As the electrons flow into the less negative electrode, zinc ions from the concentrated solution will be discharged and will plate out on the zinc. The flow of electrons through the wire prevents the establishment of equilibrium at the electrodes. As action continues the concentrations of the two solutions become more nearly the same, and the potential difference between the electrodes decreases. When the concentrations of the two solutions become equal, the potential difference becomes zero. Regardless of the difference in the concentrations of the solutions, the electromotive force of concentration cells is relatively small as compared with that of other electrochemical cells. For this reason, concentration cells are not practical sources of electrical energy.

17 The Dry Cell

This cell differs from others in containing materials that are largely in the solid state. The outside of the cell is a zinc cup, which acts as the negative electrode. This cup is lined with porous paper, which separates the zinc from the materials in the center. A carbon rod in the center of the cell acts as the other electrode. In the space around this rod there is pressed a moist mixture of ammonium chloride, manganese dioxide, a little zinc chloride, and some porous, inactive solid. The cell reaction consists in the conversion of zinc into zinc ions (oxidation) at the outer electrode, and the conversion of the ammonium ion into ammonia and hydrogen at the carbon electrode (reduction)



Since the first of these reactions leaves electrons upon the zinc, this electrode becomes the negative pole of the cell. The second reaction removes electrons from the carbon

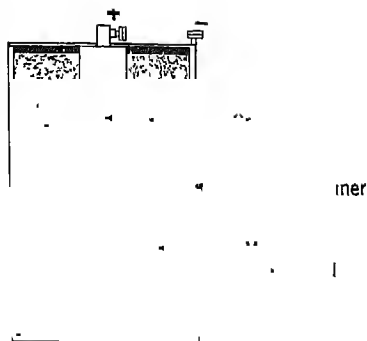


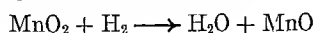
Figure 296 The Dry Cell

rod, which consequently is made the positive pole. The ammonia that is liberated reacts with the zinc ions to form complex ions ($\text{Zn}(\text{NH}_3)_4^{++}$), thus reducing the concentration of zinc ion and making it possible for the zinc electrode to become more negative.

The top of a dry cell is sealed with wax or pitch to prevent the evaporation of water. The name "dry cell" is evidently a misnomer since water is absolutely necessary in the mixture between the two electrodes. The presence of water makes possible a solution in which ammonium chloride can liberate ammonium ions, and into which the zinc ions may pass from the zinc electrode.

18 Polarization

Hydrogen collects on the carbon electrode of the dry cell and covers it with an insulating layer that increases the resistance of the cell by making it difficult for the ammonium ions to reach the electrode. Furthermore, this hydrogen sets up an electromotive force (hydrogen-electrode potential) by tending to pass into the solution as hydrogen ions. This change produces a potential difference, between the carbon electrode and the solution, that opposes the potential resulting from the discharge of ammonium ions, since the formation of hydrogen ions tends to make this electrode negative, whereas it must be the positive pole of the cell. The condition arising from the collection of hydrogen on the carbon is called *polarization*. If not prevented, polarization soon reduces the e m f of the cell to zero. Manganese dioxide is added to act as a *depolarizer* by reacting with the hydrogen which is set free



When a dry cell is used for a short time as a source of current, the hydrogen collects more rapidly than it is oxidized, the cell becomes polarized, and the e m f between the electrodes drops. During a period of rest, the hydrogen that has collected is completely oxidized, and the e m f again rises to its maximum voltage (about 1.5).

The dry cell is known as a depolarizing cell. Polarization may occur in certain other types of cells that contain no depolarizing substance. The Daniell cell is one of the non-polarizing type, since no substance is liberated at either electrode to set up an opposing e m f.

19. Metallic Couples

When a strip or rod of zinc is placed in a solution of hydrochloric acid, hydrogen is liberated on the surface of the metal, and the metal passes into the solution. We can picture the changes occurring at the point of contact between solution and zinc as follows. Atoms of zinc pass into solution as Zn^{++} ions and, as each ion is formed, two electrons are left on the metal. Hydrogen ions in contact with the metal remove these electrons and become neutral atoms of hydrogen. The atoms then form molecules, which collect in bubbles of gas and finally escape from the solution or cling to the surface of the zinc.

Let us now consider a solution of the acid in which strips of both zinc and copper are placed and are either allowed to touch or are connected by a wire. We may now observe that the zinc continues to dissolve, but hydrogen is liberated on the surface of the copper. As zinc ions are formed, electrons are left on the zinc, as before, but they are transferred to the copper where they are used to convert hydrogen ions into neutral atoms and molecules of hydrogen, it is on the surface of copper, therefore, that hydrogen is liberated.

Two metals in contact, as the copper and zinc combination that we have just described, form a *metallic couple*.

Pure zinc does not dissolve readily in hydrochloric acid, because the metal is quickly covered with a protecting layer of hydrogen that prevents the hydrogen ions from coming into contact with

the surface of the metal, which therefore maintains its negative charge. This charge on the metal prevents more zinc ions from forming, in fact, it attracts the positive zinc ions already in the solution and increases the tendency of these ions to deposit (page 632). If, in some manner, the hydrogen gas is prevented from collecting on the surface of the zinc, the hydrogen ions will remove the negative charge of the metal and thus destroy the attraction of the metal for the zinc ions in the solution. This is what happens in a metallic couple of zinc and copper.

Impure, or ordinary, grades of zinc contain small crystals of copper and other metals, and these crystals form numerous metallic couples with the zinc. Hydrogen is liberated on the surfaces of these small crystals of other metals and the zinc, with a surface left free and clean, readily dissolves.

20 Electroplating

In the manufacture of many metallic articles — tableware, hardware, plumbing fixtures — one metal is often covered with another, sometimes to protect the first metal from oxidation and sometimes to give a metal-like iron a more pleasing appearance. The article to be plated is placed in a bath containing a salt of the metal that is to be deposited. The article to be plated is made the cathode and the metal to be deposited is made the anode of the cell.

The deposit of metal must form a layer of fairly uniform thickness, and it must adhere tightly to the metal underneath. Careful control is necessary to attain this result, because the deposit may, under certain conditions, consist of large crystals, a loose powder, or a spongy mass. The character of the deposit varies with many conditions, such as the temperature, the concentration of the ions, the surfaces of the anode and cathode, and the presence of other substances in the electrolyte. In many instances substances are added to reduce the concentration of the metallic ion, thus causing the metal to plate out more slowly. The addition of potassium cyanide, KCN, to a solution of silver nitrate, for example, serves this purpose, because it forms the complex silver-

cyanide ion, $\text{Ag}(\text{CN})_2^-$, which is very slightly ionized, and thus reduces the concentration of Ag^+ ion in the solution. *Addition agents*, such as gluc, also have a pronounced effect upon the character of the layer of electroplated metal.

21. The Storage Battery

As its name implies, the storage battery acts as a cell in which energy may be stored. When the battery is charged, electrical energy is supplied and is used to produce certain substances which later may take part in an oxidation-reduction reaction, which serves to produce a difference of potential and hence makes possible the generation of an electrical current. The lead storage battery is the most familiar, and we shall use this battery to illustrate the reactions involved in storage batteries in general.

In a lead storage battery which has been discharged, both of the poles are covered with a deposit of lead sulfate (PbSO_4). The solution in the battery consists of a dilute solution of sulfuric acid. To charge the battery we connect the negative pole, or the pole which acts as the negative one when the battery is charged, to the negative end of an electrical circuit, in which there is a generator producing a direct current of about 110 volts. The positive pole of the battery is connected to the other end of this circuit. The generator, therefore, adds electrons to the pole of the battery marked A

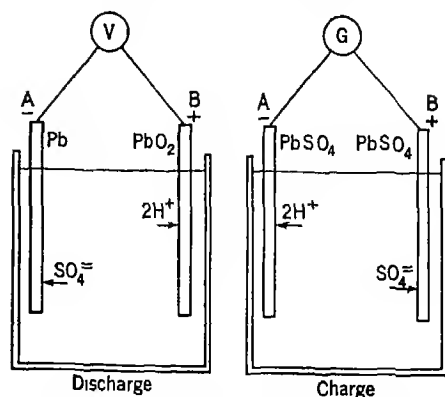
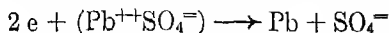
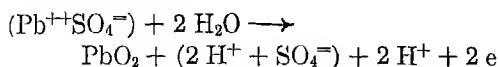


Figure 297 The Lead Storage Battery

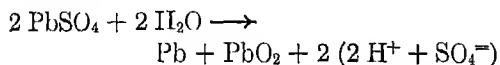
and removes them from *B*. We may assume that, at the pole marked *A*, the lead of the lead sulfate is reduced to metallic lead, and that the sulfate ion is released in the solution



At the other pole (*B*), the lead of the lead sulfate is oxidized and is deposited as lead dioxide (PbO_2), each atom of lead giving up two more electrons to the pole as this reaction takes place

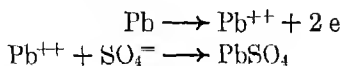


The complete reaction which occurs during charging may be represented by the following equation

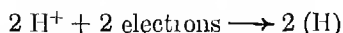


Since sulfuric acid is produced as the battery is charged, the extent to which the charging has been completed can be determined by measuring the specific gravity of the solution from time to time

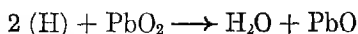
The fully charged battery may now be used as a cell to liberate electrical energy. The negative pole of the cell consists of a lead electrode, and the positive pole is the lead dioxide. During its discharge, the lead of the pole marked *A* is converted into lead ion which, in turn, is precipitated as lead sulfate, since this substance is only slightly soluble. This reaction leaves electrons on the pole where it occurs



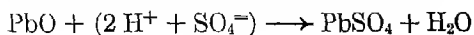
At the other pole (*B*), hydrogen ion is probably converted into free hydrogen



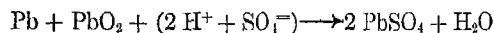
This hydrogen then reduces the lead dioxide to PbO



Lead dioxide is basic and reacts with sulfuric acid to form lead sulfate and water



The complete reaction which occurs when the battery is used to produce an electrical current is represented by the following equation

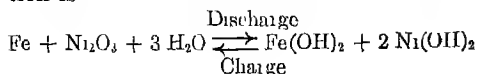


This reaction removes electrons from pole *B*. Hence, during discharge electrons flow in the external circuit from *A* to *B*. Both lead and lead dioxide are converted into insoluble lead sulfate, which is deposited on the electrodes, and the sulfuric acid is largely removed, giving a solution of lower specific gravity. The fully charged cell has a voltage of about 2.2 volts, and its solution has a specific gravity of about 1.2. The voltage of the battery, when it is ready to be charged again, is about 1.9, and the specific gravity of the solution is about 1.05. The battery may be damaged by allowing it to stand in the discharged condition; discharge should, therefore, never be complete. Damage may also result from over-charging.

The other cells which we have described in this chapter are called *primary* cells in contrast to the storage battery. In primary cells, the production of electrical energy depends upon the formation of the products of an oxidation reaction at one electrode and those of a reduction reaction at the other. There is no recharging of a primary cell, except by providing a new supply of the substances which are oxidized and reduced. In the storage battery the production of electrical energy also results from an oxidation-reduction reaction, but this reaction occurs as a sort of secondary change, following the passage of a current of electricity through the cell. This current converts inactive materials in the battery into substances which later may take part in the oxidation-reduction reaction. In other words, energy is first stored in the battery by converting electrical energy into chemical energy. Later, the chemical energy is changed again into electrical energy. This process of storing and discharging energy can be repeated over and over again.

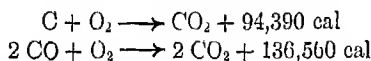
In the Edison storage battery, iron and hydrated nickel trioxide replace lead and lead dioxide as plates, and the electrolyte is a

solution of sodium hydroxide. The reaction is



Review Exercises

- 1 What are some of the ways in which the energy radiated by the sun is stored up in systems possessing relatively high free energies?
- 2 What are some of the forms of energy that may be liberated during chemical reactions or that may be consumed in reactions?
- 3 How is the heat of a reaction measured? What is the unit that is used in expressing the heats of reactions?
- 4 Calculate the heat of formation of carbon monoxide from the following data



- 5 Explain the following terms: energy of activation, calorimeter, joule, concentration cell.
- 6 Define heat, temperature, free energy change of a reaction.
- 7 A current of five amperes is passed through a solution of silver nitrate for ten minutes; the same quantity of current is also passed through a solution of cupric sulfate for five minutes. What weights of silver and copper are liberated at the cathodes in the two experiments?
- 8 What are some of the essential conditions that must be fulfilled before a chemical reaction can be used to produce a current of electricity?
- 9 Explain solution pressure of a metal. Why does it vary for different metals?
- 10 How are the positions of the metals in the electrochemical series determined?
- 11 What factors determine the electromotive force that exists between a metal and a solution of its ions?
- 12 Why do some metals have a positive electrode potential, while others have a negative potential?
- 13 Describe the hydrogen electrode and explain how it is used in determining the electrode potentials of the metals.
- 14 Calculate the electromotive force of cells

made of the following metals and solutions of their ions, assuming the concentrations of the ions are the same as those used in Table 37: nickel and copper, zinc and mercury, aluminum and copper, zinc and lead, aluminum and gold.

- 15 Draw a diagram of an electrochemical cell that might be used for the generation of an electric current from each of the reactions mentioned in question 14.
- 16 Draw a diagram of a cell that might be based upon the use of the reaction between iron and chlorine to generate an electrical current. What materials would you use as the electrodes?
- 17 Describe the construction and operation of the following cells: Daniell, gravity, concentration cell, dry cell.
- 18 Describe the construction of a lead storage battery and explain the nature of the chemical changes that occur during charging and discharging.
- 19 What causes a cell to become polarized? How is the dry cell depolarized?
- 20 In producing a substance by electrolysis, should one use a direct or alternating current? Explain.
- 21 Chlorine is produced by the electrolysis of a solution of NaCl in a cell operated at a voltage of 2.4. Calculate the cost of the energy used in the production of 10 kilograms of chlorine at 12 cents per kilowatt hour.
- 22 What weight of copper will be deposited by electrolysis when a current of 3 amperes is passed through a solution of cupric chloride, CuCl_2 , for one hour?

References for Further Reading

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- Primary Cells. *J. Chem. Ed.*, **4**, 770 (1927), **6**, 117 (1929).

THE METALS

Metallum est corpus minerale fusibile et sub malleo ex omni dimensione extensibile

GEBER

1. Introduction

The remaining chapters of this book will deal with the metals. We became familiar with the general chemical properties of these elements when we studied the alkali metals in an earlier chapter (page 375). In framing a proper definition of a *metal* we may recall, from previous discussions, that it is an element whose hydroxide acts as a base, and that its simple salts contain the element as a simple positively charged ion (cation), e.g., Na^+ . In contrast, we also recall that the hydroxides of the non-metallic elements act as acids, and that these elements are present in salts either as simple negatively charged ions, e.g., Cl^- , or as pairs of negatively charged radicals, such as SO_4^{2-} .

The atoms of the metals contain relatively small numbers of electrons — usually one, two, or three — in their outermost group, while the atoms of the non-metals have a larger number. Sodium, for example, has a single electron in its outer shell, while chlorine has seven. The metals tend, therefore, to form ionic compounds in which their atoms lose electrons, which are transferred to non-metals. The atoms of the non-metals tend to acquire electrons from metals, becoming negative ions in ionic compounds. They also often share electrons with one another, forming covalent compounds or radicals. We should also recall that, chemically speaking, there is no sharp dividing line between the metals and the non-metals. Some elements form hydroxides that act either as an acid or a base, and they appear in solu-

tions of their salts both as simple positive ions and in negatively charged radicals. Other elements that display two or more valences form compounds like those of the metals, when they are in their lower valence states, and compounds like those of the non-metals when they have higher valences.

2 The Structure of Metals

Most of the general physical properties of metals — ductility, malleability, electrical conductivity, luster, and other characteristics — can be explained by the structures of their crystals. In these crystals the atoms are closely packed, with each atom in contact with several others and all arranged in a closely packed pattern, such as the face-centered or hexagonal type of lattice (page 241). The units of the lattice are really positive ions rather than atoms of the metal. All, or at least most, of the valence electrons are separated from their atoms and are scattered throughout the crystal. These electrons are mobile and act as binding agents to hold the positive ions of the metal together. We therefore find in metallic crystals a different type of binding force than that which exists in ionic or covalent compounds. It is sometimes called metallic binding or *metallic valence*.

The difference between the crystal structure of a metal and that of an ionic compound, such as sodium chloride, is shown by Figure 128. The crystal of sodium chloride is not ductile or malleable; the ions cannot be rolled out into a sheet or drawn out into

TABLE 38

Physical Properties of Some of the Metals *

Metal	Density	Melting point °C	Boiling point °C	Specific heat	Electrical resistance	Thermal Conductivity
Aluminum	2.702	660	1800	0.217	2.62	0.461
Beryllium	1.8	1350	1500	0.397	18.5	
Bismuth	9.8	271	1450	0.030	115	0.018
Calcium	1.55	810	1200	0.149	4.6	0.221
Chromium	7.1	1615	2200	0.110	2.6	
Copper	8.92	1083	2300	0.093	1.69	0.92
Gold	19.3	1063	2600	0.032	2.4	0.744
Iron	7.86	1535	3000	0.113	10	0.141
Lead	11.34	327.5	1620	0.031	21.9	0.083
Magnesium	1.74	651	1110	0.248	4.46	0.376
Manganese	7.2	1260	1900	0.107	5	
Mercury	13.546	-38.87	356.9	0.033	95.8×10^{-6}	0.025
Molybdenum	10.2	2625	3700	0.072	4.77	0.346
Nickel	8.9	1452	2900	0.109	6.9	0.140
Platinum	21.45	1755	4300	0.032	10.5	0.167
Silver	10.5	960.5	1950	0.056 ¹	1.62	1.006
Sodium	0.97	97.5	880	0.290	4.6	0.317
Tantalum	16.6	2850	4100	0.036	15	0.130
Tin	7.31	231.85	2260	0.054	11.4	0.153
Tungsten	19.3	3370	5900	0.034	5.48	0.383
Zinc	7.14	419.4	907	0.092	6	0.265

* Heat or thermal conductivity is expressed as calories transmitted per second through metal 1 cm. thick and 1 sq. cm. in area at a temperature difference of 1° C. between the two sides of the plate. Specific heats are expressed in calories per gram per degree C. Electrical resistance is expressed as millionths of ohms of resistance by a metal cube, 1 cm. on each edge.

a wire, because the positive and negative ions occupy alternate positions, and the crystal cannot be flattened out into a thin layer without destroying this arrangement. In the crystal of a metal all the parts of the lattice are the same, and therefore they can be displaced from their original positions without destroying the crystalline arrangement, which is the same in a sheet or a small wire as it is in a large mass of the metal.

The valence electrons that bind the atoms of the crystal together must not be very firmly held, because under a difference of potential they are free to move along the metal in the direction of the positive terminal. Their places are taken by electrons that flow into the metal from the negative terminal. This movement of electrons accounts for the electrical conductivity of the metals.

3 The Occurrence of the Metals

After oxygen and silicon, the six next most abundant elements in the earth's crust are metals: aluminum, iron, calcium, sodium, potassium, and magnesium. Manganese, barium, chromium, vanadium, nickel, and strontium are the only other metals present in the earth's crust to an extent greater than 0.01 per cent. The importance of these elements as free metals, however, does not depend upon their relative abundance as a part of the earth's crust. Instead, their importance is determined by the occurrence of the free metal, or its compounds, in deposits at least moderately rich in metal-content, upon the ease with which these deposits can be converted into the metal, and upon the useful properties of the metal. It happens, therefore, that some of our most widely used metals are not very abundant in nature,

while others that are relatively abundant are used very little. Until practical and inexpensive methods of producing metallic aluminum from some of the compounds in which the element occurs in nature were discovered not many years ago, very little aluminum was produced, although it is the most abundant of the metals. Even yet, aluminum is produced from relatively rare mineral sources and not from clay and various kinds of rocks in which most of the aluminum of the earth's crust occurs. Four of the most abundant metals (sodium, potassium, calcium, and magnesium) have limited uses as metals first, because they are not easily prepared from their compounds, and second, because the metals do not lend themselves to the purposes for which metals usually serve. They are not durable and are entirely unsuited for the manufacture of metallic articles or for the construction of metallic structures of any kind. Alloys containing some of these metals are more useful than the metals themselves.

Silver and gold, which occur as native metals in nature, were used at least 8000 years ago, chiefly in making ornaments. Of the metals that occur as compounds, copper and tin were very early produced by the reduction of their oxides with carbon or carbonaceous material. An alloy of these two metals was also produced at least 5000 years ago. This alloy is called *bronze*. The discovery of how to produce it marked the beginning of the "bronze" age. Although iron is produced very easily from its ores, not until long after the time when brass and bronze had been produced did man learn of its great usefulness and of means of producing it. The very extensive development of the automobile industry and the railroads, and the wide use of machinery and tools of every kind, have made iron and its alloys, and also non-ferrous metals and their alloys, extremely valuable and important commodities. For ours is the "machine age," and we could have very few machines without metals from which to construct them. The

many uses that require metals have stimulated the search for economical methods of reducing the metals from their ores. When the pure metals have not met the requirements, alloys of many kinds have been made to provide a metal with the properties required for a specific need. Thus, there has been produced brass harder than copper, steels that are tough and strong, steels that are resistant to chemical action, steels that are impermeable to hydrogen, steels that do not lose their "temper" when heated, stainless steels; gold alloys harder than pure gold, and colored green, white, or pink, and alloys of many kinds that withstand the wear and tear of moving gears and bearings more satisfactory than any pure metal.

4. Ores of Metals

Ores are the natural materials in which metals or their compounds occur in the earth. They usually contain large percentages of worthless earthy material, called *gangue*. Some of the least active metals are often found in the free state. These are said to be *native ores*. We have already (page 520) described the occurrence of native arsenic, antimony, and bismuth. Gold, silver, platinum, and copper also occur in the free state.

The most important classes of ores, in addition to native ores, are listed below.

(1) *Oxides*. This constitutes one of the most important groups of ores. Oxides are important natural sources of iron, aluminum, manganese, and tin.

(2) *Sulfides*. Ores containing the sulfides of the metals are important sources of zinc, cadmium, mercury, copper, lead, nickel, cobalt, silver, arsenic, and antimony.

(3) *Carbonates*. Iron, lead, zinc, and copper occur as carbonates, and ores containing these compounds are important sources of these elements. They are not so important, however, as the oxide or sulfide ores of the same metals. Calcium, magnesium, barium, and strontium also occur in nature as carbonates.

(4) *Sulfates*. Calcium, barium, and strontium occur abundantly as sulfates. A minor ore of

lead contains lead sulfate. Sodium sulfate also occurs in nature.

(5) *Halides* The chlorides of sodium and potassium occur in nature and are important sources of these metals and their compounds. Calcium fluoride (fluorspar) serves as the principal source of fluorine, but is of little significance as a source of calcium. Sodium aluminum fluoride, or cryolite (Na_3AlF_6), is extensively used in the production of aluminum. Silver occurs as the chloride (horn silver). Small amounts of the bromides and iodides of sodium, potassium, and magnesium are usually associated with natural occurrences of sodium chloride. These sources also contain some magnesium chloride.

(6) *Silicates* Silicates of aluminum, calcium, potassium, sodium, and magnesium are very abundant, and silicates containing many other metals (page 534) are well known. With the exception of two or three cases, however, the naturally occurring silicates are of little value as the sources of the metals which they contain. They are so difficult to decompose that the recovery of the metals from them is not economical.

(7) *Other Ores* In addition to the groups of ores listed above, several of the metals occur in unusual kinds of compounds. We shall mention only a few of these to indicate the wide variation in the types of compounds found in nature. Sodium and potassium sometimes occur as nitrates, gold is sometimes found in the form of a telluride, chromium occurs as ferrous chromite, $\text{Fe}(\text{CrO}_2)_2$, which is the most important ore of this element, molybdenum is found as the lead salt of molybdic acid, PbMoO_4 , and the principal ore of tungsten is ferrous tungstate, FeWO_4 . Most of these miscellaneous ores are used to produce some of the rarer and less extensively used metals. The most important ores of the most widely used metals are oxides, sulfides, and carbonates.

METALLURGY

Metallurgy deals with the various processes used in the production of metals from their ores. Most of these processes involve chemical reactions, but before such reactions can be used, there must be *preliminary treatments* to remove a considerable portion of the worthless material and to concentrate that part of the ore which contains the metal.

These treatments are followed by *smelting*, and the metal is finally purified by a process of *refining*.

In the course of the preliminary treatment, the ore is first crushed and sometimes ground to a powder. This material is then separated into two or more fractions by various methods. We have already (page 555) described the oil flotation method of concentrating ores. Separation may also be effected by taking advantage of differences in the rates at which various kinds of particles settle in water. If the particles containing the metal are attracted by a magnet, they can be separated by passing the crushed ore, on a continuously revolving belt or screen, beneath a large electromagnet or a series of magnets. Shaking tables may also be used, if the particles containing the metals are heavier than those composed of worthless materials. Cottrell electrical precipitators (page 551), or devices based upon the same principle, are sometimes used to separate parts of the ores that readily become charged, when brought into a strong electrical field, from materials not readily charged. The charged particles are attracted to the highly charged metallic plates of the device, where they are discharged.

The preliminary treatment of the ore may also include certain chemical changes by which the compounds contained in the ore are converted into substances that are more easily reduced. Most sulfide ores, for example, are "roasted." The ores are heated in the air to convert the sulfides into oxides of the metals, and to remove the sulfur as sulfur dioxide. Ores containing water chemically combined in hydrates, or ores containing carbonates of the metals, are usually heated to expel the water and to decompose the carbonates by liberating carbon dioxide.

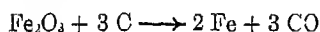
After the preliminary treatment, the ore is ready for reduction in the *smelter*. This is a furnace in which the metal is produced in large quantities and from which it is drawn off in the liquid condition. Since most ores contain considerable quantities of gangue,

even after concentration by the preliminary treatment, a *flux* is added to convert the *gangue* — the worthless material — into a *slag*. Since the gangue is usually silica or silicates, a basic flux is added. This is usually lime or limestone, which reacts with silica to produce calcium silicate. Conversely, if the gangue is a basic substance, such as lime or limestone, which produces lime upon heating, an acid flux, usually silica, is added. The slag must be a substance which is easily melted and which separates from the fused metal, preferably by forming a top layer to protect the metal from oxidation. As it collects, it can be drawn off from the furnace from time to time.

5 Metallurgical Methods

For the present, we shall consider only the most important general types of reactions employed in the reduction of metals from their ores.

(1) The oxide ores are usually reduced by carbon. This is the method used, for example, in the production of iron.



Either carbon monoxide or carbon dioxide may be produced, depending upon the temperature to which the charge of the furnace is heated and the quantity of air supplied. If carbon monoxide is produced at first, it may cause further reduction.

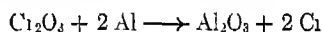


Carbon is often used as the reducing agent not only for those ores that occur as oxides, but for the oxides that are produced by roasting the sulfide ores.

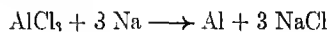
(2) Metals that occur in the free state are separated from the gangue of their ores by heating until the metals are melted, or by adding substances in which the metal dissolves. By one or the other of these methods the metal may be separated from the infusible or insoluble portions of the ores.

(3) Aluminum is used to reduce some oxides. Carbon is not a satisfactory reducing agent for some metals because of its tendency to combine

with them, forming carbides, and also because its use requires excessively high temperatures. Reduction by aluminum is used to produce chromium and manganese and also to reduce iron in small quantities in cases where two pieces of steel are to be welded together. The high temperature required to melt the ends of the steel pieces which are to be welded is furnished by the reaction itself. The mixture containing the oxide of the metal and the aluminum powder that reduces it is called *thermit*. This method of reducing metallic oxides was developed by Goldschmidt, and so the process is called either the *thermit* or the *Goldschmidt process*. The thermit is placed in a dry fire-clay crucible, which is embedded in sand. A small amount of an ignition mixture is placed in a small depression in the top of the mass. This starting mixture, which contains barium peroxide and powdered magnesium, is itself ignited by means of a burning strip of magnesium ribbon, which is placed in the mixture and ignited. The reaction produces enough heat to melt the metal, which collects in the bottom of the crucible with the aluminum oxide on top. A typical reaction involving the Goldschmidt process is shown by the following equation for the reduction of chromium trioxide.



(4) Other reducing agents are used in special cases. Sodium, potassium, and magnesium may be used to reduce the oxides or chlorides of less active metals. Thus, aluminum was at one time produced by reducing aluminum chloride with metallic sodium.



Hydrogen may also be used in some cases (page 115). Iron is sometimes used to reduce stibnite, Sb_2S_3 . Free antimony and ferrous sulfide are produced by this reaction.

(5) Electricity may be used in metallurgy for two purposes. (a) It may be used to provide the heat necessary for the reaction and for the melting of the products. In these cases the ores are smelted in an electric furnace, and carbon is added to act as the reducing agent. (b) Electricity is also used more directly in the recovery of certain metals by employing it in electrolytic processes. Electrolytic methods are used to produce sodium, potassium, calcium, magnesium, and aluminum. Since in many cases the metals

would react with water if they were deposited from aqueous solutions, baths of fused salts, fused hydroxides, or solutions containing some compound of the metal dissolved in one of its fused salts are used. Thus, calcium may be deposited by the electrolysis of its fused chloride, sodium by the electrolysis of the fused hydroxide, and aluminum by the electrolysis of a bath containing aluminum oxide dissolved in fused cryolite, Na_3AlF_6 . The passage of the electric current serves both to discharge the ions of the metal and to maintain the temperature at the point required for the fusion of the electrolyte.

6. Refining

The metals produced directly in most metallurgical processes require further purification. They usually contain portions of slag, dissolved gases, and other metals that have been reduced simultaneously. These impurities are not always undesirable, but usually further refining is necessary in order that the metal may possess all of the qualities that fit it for the purpose for which it is produced.

Since refining consists in separating the metal from the impurities that it contains, advantage is taken of differences in melting point, volatility, ease of oxidation, and similar factors. Electrolysis is also widely used in the refining of many metals, such as gold, copper, lead, zinc, aluminum, and chromium. Some ores are leached with solutions that dissolve the metals. These solutions are then electrolyzed. In other cases, the impure metal is used as the anode in an electrolytic cell containing a solution of a salt of the metal. The refined metal is deposited on the cathode, which is made of pure metal of the same kind.

ALLOYS

When two or more metals are melted together and the mass is cooled, the solid that forms is called an *alloy*. We find very few metals in their pure state in the metallic articles that are familiar to everyone. Coins, jewelry, silver plate, the metallic parts of

automobiles, tools, ornaments, dishes, all these are made of alloys. Large quantities of nearly pure copper, iron, and aluminum are used, but in most iron, particularly, small quantities — and sometimes considerable quantities — of other elements are added in order that the iron may possess the properties that fit it for special uses. Various kinds of steel are alloys of iron with nickel, manganese, tungsten, chromium and other metals. They also usually contain certain percentages of carbon, silicon, and traces of other non-metals.

7 The Composition and Nature of Alloys

Alloys are prepared by mixing two or more metals in their liquid states. These liquids behave in the same way as other liquids under similar conditions. They may mix in all proportions, they may mix in certain proportions; or they may separate into different layers without mixing at all. They may also react chemically with each other to produce compounds. When the mixture cools, the composition of the solid that forms depends largely upon the relations that existed between the metals in the liquid mixture.



Courtesy of the International Nickel Company, Inc.

Figure 298 Alloys Are Used in Heavy Construction Equipment

Welded plates of low alloy high tensile nickel-copper-manganese steel give strength without adding weight to the frame. Principal shafts and gears are of nickel-chromium-molybdenum steel, heat treated.

ture The composition of alloys may, therefore, show the following differences (1) The crystals may be those of the pure metals, which are segregated as solidification occurs. (2) If the metals form a solution in the fused state, they may give a solid solution upon cooling (3) If the metals react, the alloy will contain crystals of their compounds Many alloys contain two, or even all three, of these states of their components Strictly speaking, the term *alloy* refers to solid solutions of metals, but the common use of the term allows it to be applied to all kinds of solid metallic materials containing two or more metals

8 Eutectic Mixtures

In order that we may understand the changes that occur when solutions composed of liquid metals solidify, let us consider a mixture of two metals, such as antimony and lead These metals form a solution of one in the other, when the metals are heated together A small quantity of antimony can be dissolved in a large quantity of lead, or vice versa Upon cooling, crystals of lead form at first, if this metal is present in very much larger quantities than antimony If a small amount of lead has been dissolved in a relatively large quantity of antimony, crystals of antimony separate as the solution cools In either case, the temperature at which the pure metal crystallizes is lower than the temperature at which it would crystallize if the other metal were absent The melting point of pure lead is 327°C . and that of pure antimony is 630.5°C In Figure 298, temperature is plotted vertically and the composition of the alloy is plotted horizontally along the bottom line If either metal is melted and the other is added to it in relatively small amounts, the freezing point is lowered by an amount which increases with the concentration of the second metal The shorter curve shows the different temperatures at which lead freezes from solutions containing different percentages of antimony If we drop a perpendicular line

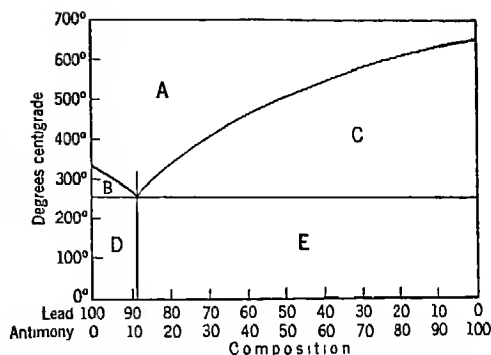


Figure 299 Lead-Antimony Alloy Diagram

from any point on this curve to the line at the bottom, the intersection will represent the composition of the lead-antimony solution from which pure lead will crystallize at the temperature corresponding to the point on the curve The longer curve shows the effect of increasing amounts of lead upon the freezing point of antimony If a perpendicular line is drawn from the point where these two curves meet to the bottom line, the point of intersection indicates the composition of a mixture from which both lead and antimony will crystallize at the temperature (247°) corresponding to this point This temperature is called the *eutectic temperature* and the mixture of metals is called the *eutectic*. It is evident that this mixture has a lower freezing point than any other solution of lead and antimony

Let us consider a liquid mixture at a temperature of 600° or higher and composed of 60 per cent antimony and 40 per cent lead Let us now assume that the mixture is cooled until solidification begins The first crystals will be those of pure antimony As antimony is removed from the solution, the concentration of lead will increase and the freezing point of antimony will be reduced, dropping along the curve Finally, the freezing point of antimony will be reduced to the temperature corresponding to the eutectic But lead also freezes at this temperature from the same solution, consequently, the concentration of the liquid mixture will no longer change The composition of the mass of crystals which form and that of the liquid will remain the same until

solidification is complete. Region B in the diagram represents a mixture of lead crystals in melted lead-antimony; C, antimony crystals in melted lead-antimony; D, lead crystals and solid eutectic; E, antimony crystals and solid eutectic; and A, a mixture of the two metals in the liquid state.

TABLE 39

A Few Alloys

Composition (per cent)	Trade name
90 Al, 10 Mg	Magnalium
98 Al, 1.25 Mn	Aluminum Alloy 35
40-80 Co, 20-35 Cr, 0-25 W, 0.75-2.5 C	Stellite
89 Cu, 9 Zn, 2 Pb	Hardware bronze
75 Ni, 12 Fe, 11 Cr, 2 Mn	Nichrome
82 Cu, 15 Mn, 3 Ni	Manganin
55 Cu, 18 Ni, 27 Zn	Nickel silver
60 Cu, 40 Ni	Constantan
90 Cu, 10 Sn	Gun metal bronze
85 Cu, 15 Zn	Red brass
67 Cu, 33 Zn	Yellow brass
60 Cu, 25 Zn, 15 Ni	German silver
90 Au, 10 Pd	White gold
80 Au, 20 Pd	Palau
60 Au, 40 Pt	White gold
75 Au, 10-20 Ag, 5-15 Cu	18 carat gold
74 Fe, 18 Cr, 8 Ni, 0.18 C	Stainless N
60 Ni, 33 Cu, 6.5 Fe	Monel

We are not to assume, however, that all alloys are eutectic mixtures. Some are approximately of the same composition as the eutectic. Unless the mixture of metals in the liquid state has exactly the composition of the eutectic, it is evident that the solidified mass must contain segregated crystals of one of the metals. The metal present in excess must crystallize alone before the eutectic temperature is reached. It very often happens, as mentioned previously, that the solidified mass may contain, also, crystals of a compound of the metals or their solid solution. In general, it may be said that an alloy which is as near the eutectic in composition as possible, has the most homogeneous, fine-grained structure and is the most serviceable.

9 Properties of Alloys

The properties of an alloy cannot be pre-

dicted from its composition. As shown above, the freezing or melting point of a binary alloy may be lower than that of either component, but this is not always true. Amalgams, which are alloys containing mercury, are usually solids at ordinary temperatures, although mercury itself is a liquid at these same temperatures and does not freeze until it is cooled to -39°C . If the alloy is composed essentially of a solid solution, it may melt at a temperature which is between the melting points of its components.

The hardness of an alloy is usually greater than that of the pure metals composing the alloy. The color, sometimes, is what we might expect from a mixture of two metals of different colors. Brass is made less red than copper by the presence of zinc, but often the color of the alloy fails to reveal the effect of the color of one metal, and it may be entirely different from that of either. A five-cent piece does not show by its color that it contains any copper, and silver and gold may be alloyed to form "green gold." The alloy is usually a poorer conductor of electricity than its components. In general, it is more resistant to chemical changes, such as corrosion. If the alloy contains compounds of metals with each other, or compounds of metals with non-metals, its properties are usually very much different from those of its components.

10 The Structure of Alloys

The structure of an alloy depends upon several conditions. When a solution of fused metals cools, crystals of one metal form at first, and the solution becomes less rich in that component. As cooling continues, the crystals of the first metal that separates become larger. Finally, the eutectic temperature and the eutectic composition of the solution are reached. At this point, the solution remaining crystallizes, usually, as small crystals of both metals. Hence, alloys made in this manner usually contain large crystals of one metal embedded in a matrix of very small crystals of the eutectic mixture. Alloys

made by rapid cooling and from mixtures having a composition near that of the eutectic mixture are usually composed of small crystals and have a fairly homogeneous structure. These are characteristics that are desirable in many alloys.

COMPOUNDS OF METALS

The most important compounds of the metals can be classified as oxides, hydroxides, and salts. The oxides of the metals above mercury in the electrochemical series may be prepared by allowing the metal to react directly with oxygen. They may also be prepared by heating the hydroxides of all the metals below barium. The oxides of all the metals except those of the alkali family can be prepared by decomposing the carbonates or nitrates. The hydroxides of all the metals, except the alkali metals, barium, and to a lesser extent, strontium and calcium, are slightly soluble and can be prepared by adding sodium hydroxide to a solution of a salt of the metal. A few of the hydroxides can be prepared by treating the oxides with water, this is true, for example, for the oxides of calcium, strontium, barium, and magnesium.

11 Salts of Metals

The salts of the metals are prepared by many different kinds of reactions. The following summary lists some of the most common ways of producing them.

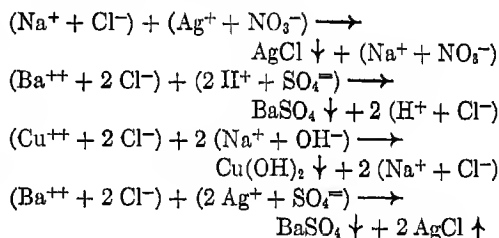
(1) *Action of Acids* Salts may be formed by the action of the appropriate acids upon the oxide, hydroxide, carbonate, sulfide, or sulfite of the metal. Certain metals may also be converted into salts directly by allowing them to react with acids. As examples of reactions of this kind, we may recall the formation of zinc chloride when zinc reacts with hydrochloric acid, of cupric nitrate when copper dissolves in nitric acid, and of cupric sulfate when hot concentrated sulfuric acid acts upon copper.

(2) *Direct Combination* Some salts are easily prepared by heating metals and non-metals. Many metals combine directly with chlorine to form chlorides, with bromine to form bromides, and with iodine to form iodides. They also combine upon heating with sulfur.

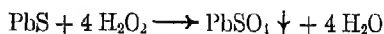
(3) *Liberation of Volatile Acids* We have noted several instances in which a non-volatile acid

liberates a volatile acid from its salts. Thus, sulfuric acid will liberate hydrochloric acid from chlorides, acetic acid from acetates, nitric acid from nitrates, hydrofluoric acid from fluorides, and so on. In each of these cases, a salt of the strong acid is produced. The escape of the volatile acids causes these reactions to run to completion. If water is present and if the volatile acid is soluble in it under the conditions employed, the reaction is not complete and proceeds only until equilibrium is attained.

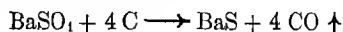
(4) *Precipitation Methods* Double decomposition reactions may be used to produce new salts from (a) two original salts, (b) a salt and an acid, or (c) a salt and a base. If one of the products of the reaction is only slightly soluble in the medium, it will precipitate, causing the reaction to be more complete and making it possible to separate the two products from each other by filtration. If both products precipitate, the reaction may be even more nearly completed, but the separation of the products is likely to prove difficult. Examples of reactions that produce salts by double decomposition are given below.



(5) *Reduction and Oxidation* The direct combination of metals with non-metals is, of course, an example of salt formation by oxidation and reduction. We refer here, however, to other cases of oxidation and reduction in which compounds of metals, which may be salts themselves, are oxidized or reduced. Thus, lead sulfide may be oxidized by hydrogen peroxide to form lead sulfate.



Barium sulfate is reduced, when it is heated with carbon, to barium sulfide.



Potassium permanganate is reduced to manganous chloride (MnCl_2) by the action of HCl.

(6) *Fusions* Double decomposition reactions

TABLE 40

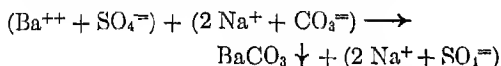
The Solubility of Salts

Anion	Na	K	NH ₄	Mg	Ca	Sr	Ba	Al	Cr	Zn	Fe	Ni	Co	Mn	Cu	Bi	Hg(-ic)	Cd	Sn	Ag	Pb	Hg(-ous)
Nitrate	-----	-----	-----	-----	-----	-----	-----	all soluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Acetate	-----	-----	-----	-----	-----	-----	-----	all soluble (silver acetate is only moderately soluble)	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Chloride	-----	-----	-----	-----	soluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	insoluble *	-----	-----
Sulfate	soluble	-----	-----	-----	insoluble	-----	-----	-----	-----	-----	soluble	-----	-----	-----	-----	-----	-----	-----	-----	(ins)	-----	-----
Carbonate	soluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	insoluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Phosphate	soluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	insoluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Silicate	soluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	insoluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Sulfide	soluble	-----	-----	-----	-----	-----	-----	-----	-----	-----	insoluble **	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

* Lead chloride is moderately soluble

** The sulfides of Mg, Ba, Ca, Sr, Al, and Cr are strongly hydrolyzed by water, the sulfides of the first four of these metals form soluble acid sulfides, while the sulfides of Al and Cr are converted into insoluble hydroxides. In other cases hydrolysis may result in the formation of insoluble compounds, thus, the hydrolysis of bismuth chloride, which is soluble produces insoluble bismuth oxychloride, BiOCl ----- soluble, ----- insoluble

may occur when certain solid substances are heated together until they melt. The melted mass acts as a solution of one salt in the other. Let us consider the reaction between barium sulfate and sodium carbonate. The former dissolves only very slightly in water. Consequently, there is very little opportunity for a double decomposition between these two substances, when barium sulfate is treated with an aqueous solution of sodium carbonate. But if the two substances are mixed in the dry state and heated, we find that the barium sulfate dissolves more readily in the melted sodium carbonate than it does in water. A reaction consequently occurs, and sodium sulfate and barium carbonate are formed. The latter is not soluble in the melt, and its precipitation helps the reaction to go to completion.



If the fused mass is allowed to cool and is then placed in hot water, the two products can be separated. The sodium sulfate dissolves and the barium carbonate does not. The latter may be removed by filtration, and can be treated with acids to form other desired salts, such as the chloride, nitrate, or acetate of barium. This procedure is often used in converting insoluble salts of the metals, such as barium sulfate, into soluble compounds, which can then be detected by analytical tests, or which may be used, on a larger scale, for commercial or laboratory purposes.

12. Important Classes of Salts

The anions found in the most widely used salts of the metals are few in number. The most extensively used salts of the metals are nitrates, chlorides, sulfates, acetates, carbonates, phosphates, sulfides, and silicates. The solubilities of these salts in water vary greatly, although it is possible to classify them as relatively soluble or relatively slightly soluble, and thus we have attempted to do in the accompanying table (Table 40). Familiarity with the general solubility relations shown in this table is of extreme importance to the chemist or to the student of chemistry. With the help of this information it is possible to predict whether double decomposition reactions involving these salts will occur or how complete such reactions will be. This information is also helpful in deciding the methods to be employed in

the production of these salts, and also in producing other substances from them.

Review Exercises

1. Summarize the principal differences between the elements that are classified as metals and those that are classified as non-metals. Consider chemical properties and atomic structures.
2. Define ore, gangue, flux, slag.
3. Describe some of the methods that are most generally used in the production of metals from their ores.
4. What factors determine the amount of a metal that is used? Illustrate by referring to the production of the following metals: iron, aluminum, sodium, and copper.
5. Why is aluminum more expensive than zinc?
6. What is an alloy? How do alloys differ from one another in composition?
7. Define eutectic mixture. Starting with a mixture containing equal weights of lead and antimony at a temperature of 600° , describe the nature of the crystals that form as the mixture is cooled.
8. Starting with barium sulfate, describe the methods that you would use in preparing barium acetate.
9. Describe the methods that you would use in converting the following substances into the products indicated: sodium chloride into sodium sulfate, silver nitrate into silver chloride, barium chloride into barium sulfate, calcium carbonate into calcium nitrate, and sodium carbonate into sodium sulfate.
10. How would you separate sodium chloride from silver chloride? Starting with a solution containing lead (Pb^{++}) and cupric (Cu^{++}) ions, what reagent could you add that would precipitate the lead ions from the solution without precipitating the cupric ions?
11. What does the extent of hydrolysis of the chloride of a metal indicate concerning the strength of the metal's hydroxide as a base and the general basic character of the metal?
12. The solubility of barium sulfate at 18° is 0.00001 g/mol wt per liter. What weight in grams of barium sulfate is contained in 100 ml of a saturated solution?
13. A solution at 18° contains 0.01 g atomic

weight of barium, as Ba^{++} ions, per liter and an equal concentration of sulfate ion. What is the weight of the precipitate of barium sulfate that forms in one liter of this solution?

- 14 A solution containing barium chloride is treated with a solution of sodium sulfate, and the precipitate of barium sulfate is removed by filtration. If the concentration of the sulfate ion in the filtrate (at 18°) is 0.001 g ion weight of SO_4^{--} per liter, what is the concentration of the barium ion in the same solution?
- 15 Refer to Table 38 (page 642) and answer the following
 - (a) Which feels colder to the hand, lead or silver?
 - (b) Which would liberate more heat when cooled 10° , 1 g of bismuth or 1 g of iron?
 - (c) What metal is a better conductor of electricity than copper?
 - (d) Which would serve better as resistance in an electric heater, silver or molybdenum?
 - (e) What two desirable properties does tungsten have as a filament in an electric light bulb?
- 16 Starting with a solution that contains the nitrates of barium, silver, and nickel, what ions would you add to precipitate first silver, then nickel, and finally barium? What ion (anion) could you add to the mixture that would precipitate barium only?
- 17 Barium sulfate does not dissolve in a solution

containing hydrochloric acid but barium carbonate does. Explain.

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THE ALKALINE EARTH METALS

The atomic weight of magnesia as determined by Dr Thomson is 20. Consequently this alkaline base is composed of magnesium 12, or one atom, and oxygen 8, or one atom.

TURNER, 1828

(Illustrative of the confusion existing in the early nineteenth century)

1 Introduction

In the early days of chemistry the substances now recognized as slightly soluble oxides of metals, such as Fe_2O_3 , were called "earths." A few of these "earths" were known to form alkaline mixtures with water and, in general, to resemble the alkalis. For this reason they were called the *alkaline earths*. Until the early part of the nineteenth century, the alkaline earths were thought to be elements. In 1808, Davy showed that this idea was erroneous, and that these earths, or rather the corresponding hydroxides, can be decomposed electrolytically, in the same manner that sodium hydroxide (page 377) is decomposed to form metallic sodium. By electrolyzing the fused hydroxides of the alkaline earths, Davy produced four metals, which he called *calcium*, *strontium*, *magnesium*, and *barium*. These elements, together with beryllium and radium, are the metals to be studied in this chapter.

The relationship between beryllium or magnesium and the other metals of the family is somewhat obscure. Frequently, these two elements are placed in the B division of group two along with zinc, cadmium, and mercury. Their atomic structures, however, show that they are more closely related to calcium, strontium, and barium, than to zinc, cadmium, and mercury. Structurally,

all the metals of the A division of this group, including beryllium, magnesium, and radium are characterized by two electrons in the outermost level. Furthermore, in the atoms of each of these elements, the level next to the one on the outside is composed of a stable group of eight electrons (two for beryllium), a group like that found in the outer shell of the atom of one of the inert gases. This is not true of the atomic structures of the B division elements, in which the outer shell, after the removal of the valence electrons, contains eighteen electrons instead of eight.

2 General Physical Properties

The elements of this family are decidedly metallic in appearance and in their general physical properties. They have a bright white luster on newly prepared surfaces, but they readily tarnish in air or oxygen. Beryllium and magnesium, however, tarnish less readily than the others. All the metals of this group are relatively light, the density of the heaviest (radium) being less than that of iron, nickel, copper, or zinc. They are good conductors of the electric current, and although somewhat brittle, they are ductile and malleable to a certain extent. In general, they are not so soft as the alkali metals. Beryllium is very hard, but the hardness of

the metals of the family decreases with increasing atomic weight

3 General Chemical Properties

Each of the metals has only one valence, positive 2. They form oxides corresponding to the formula XO , hydroxides $X(OH)_2$, and salts XCl_2 . The hydroxides are basic and never acidic, except beryllium hydroxide, which is amphoteric. The oxides of the five heaviest metals of the family react readily with water to form hydroxides, which are increasingly soluble and possess more strongly basic properties as the atomic weights of the metals increase. Magnesium oxide reacts slowly with water, and the hydroxide is less soluble and acts as a weaker base than calcium hydroxide. Barium hydroxide is more soluble and acts as a stronger base than the hydroxides of magnesium, calcium, and strontium, in a 0.1 N solution it is apparently 77 per cent ionized. Beryllium oxide does not react with water.

The activity of the metals, themselves, also increases with increasing atomic weight. Magnesium decomposes cold water slowly, but barium reacts very much more rapidly. Corresponding to the increase in activity the electrical potential between the metal and its ion also increases with increasing atomic weight. The electrode potential for magnesium is 1.9 volts, while for barium it is almost as great as for potassium, 2.9 volts. All of the metals will burn in oxygen or in air, when heated. They also react with nitrogen to form nitrides. They combine readily with many of the non-metals, such as sulfur and the halogens. They also liberate hydrogen from non-oxidizing acids, and beryllium, because of its amphoteric character, liberates hydrogen from sodium hydroxide.

4 Occurrence

None of these metals occur free in nature because of the extreme ease with which they combine with other elements. The most

abundant compounds of each metal are listed below

5 Beryllium

The most important mineral containing this element is *beryl*, beryllium aluminum silicate. When this mineral contains chromium it is colored green and is called *emerald*.

6. Magnesium and Calcium

These two metals are much more abundant in the earth's crust than the others of this family. They are found in *limestone*, $CaCO_3$, *dolomite*, $MgCO_3 \cdot CaCO_3$, *magnesite*, $MgCO_3$, *talc*, $H_2Mg_3(SiO_3)_4$, *fluor spar*, CaF_2 ; *asbestos*, $CaMg_3(SiO_3)_4$, *gypsum*, $CaSO_4 \cdot 2H_2O$, *Meerschaum*, a hydrated magnesium silicate, and *spinel* (magnesium aluminate). Magnesium and calcium salts are also present in sea water and in deposits of salts which have been formed by the evaporation of sea water. Calcium, and magnesium to a much smaller extent, are found in various plant and animal structures and products. Bones contain calcium phosphate as their essential organic constituent.

7. Strontium and Barium

Strontium occurs principally as *celestite*, $SrSO_4$, and *strontianite*, $SrCO_3$. *Barium* occurs in nature as *barite*, $BaSO_4$, and *witherite*, $BaCO_3$. The occurrence of radium has been described previously (page 263).

PRODUCTION AND USES OF THE METALS

8. Production of Beryllium

Since pure beryllium is of little use, an alloy, especially an alloy with copper, is usually produced commercially instead of the pure metal. First, beryllium oxide must be produced from the ore, *beryl*, which is a silicate of aluminum and beryllium. The ore is heated until it begins to melt and is then cooled quickly by pouring into cold water. The mass is then treated with sulfuric acid, which forms the sulfates of aluminum and beryllium. Water and ammonium sulfate

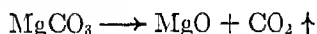
are added, and as the solution is evaporated, crystals of the alum, ammonium aluminum sulfate, are formed. These crystals are removed, and the beryllium sulfate is then crystallized by further evaporation of the solution. The sulfate is then converted into the hydroxide, which when heated forms the oxide. An alloy of copper and beryllium is made by reducing the oxide in an electric furnace by means of coke. Copper, or an oxide of copper, is added at the same time.

Beryllium itself can be produced by the electrolysis of fused beryllium chloride or of a fused mixture of the oxide and fluoride.

9. Production of Magnesium

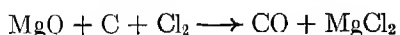
This metal was first produced commercially by the electrolysis of fused magnesium chloride, which was obtained largely from the brines of salt wells. It is now produced by several different methods from magnesite, dolomite, and from magnesium chloride obtained by a series of reactions from the magnesium ions in sea water.

Two processes are used to produce magnesium from magnesite. In each process the magnesite is first converted into magnesium oxide by calcination



The oxide is then reduced by powdered coal at a temperature somewhat above 2000° . As magnesium is produced, it vaporizes, and the vapor, upon cooling in an atmosphere of hydrogen, forms small crystals of rather impure magnesium. The metal is purified by distillation under greatly reduced pressure.

In the second process, the magnesium oxide produced from magnesite is heated with coal, and chlorine is passed over the mass. The following reaction occurs



The magnesium chloride is purified, and it is then electrolyzed to produce metallic magnesium.

Dolomite is calcined to produce calcium and magnesium oxides, which are then

heated with ferrosilicon in an electric furnace. Silicon reduces magnesium oxide to the metal and forms silicon dioxide, which reacts with calcium oxide to form calcium silicate. The magnesium vaporizes as it is produced, and the crystals that form upon cooling are purified by distillation under greatly reduced pressure.

In the production of magnesium from sea water, magnesium hydroxide is first produced by treating sea water with milk of lime, $\text{Ca}(\text{OH})_2$. The magnesium hydroxide that precipitates as a result of this treatment is recovered by means of suction filters. The residue is then mixed with a concentrated solution of magnesium chloride, and finally it is treated with hydrochloric acid, which converts the hydroxide into chloride. Magnesium chloride is then purified by a series of evaporations and crystallizations, and the pure, fused chloride is electrolyzed. The melted magnesium is removed from the cells in ladles and poured into molds, where it solidifies as bars, the purity of which is about 99.9 per cent. Sodium and potassium chlorides may be added to lower the melting point of the bath.

10. Production of Calcium, Strontium, and Barium

These metals are produced by the electrolysis of their fused chlorides or fluorides. The production of calcium in a simple electric cell is shown in Figure 300. The salts of the metal are melted in a graphite vessel, which serves as the anode. The cathode is made of iron and dips just below the surface of the liquid. Calcium is deposited on the iron cathode and is made to form a stick of the metal when the cathode is slowly raised as electrolysis proceeds. This stick of calcium acts, therefore, as the cathode of the cell. In the cells used to produce metallic calcium in large quantities, graphite anodes are suspended in the bath of fused calcium chloride. The metallic calcium is deposited on the top of an iron cathode, which is continuously raised as electrolysis proceeds, or it is liberated on an iron cathode in the bottom of the

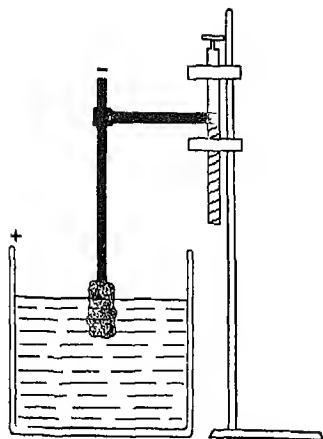


Figure 300 The Preparation of Metallic Calcium

cell, from which it rises as globules of the melted metal and is collected by being caused to solidify on a block of calcium which is slowly raised.

The method of producing *strontium* is, in general, the same as for calcium, but the preparation is much more difficult. Metallic *barium* is usually prepared by the electrolysis of fused barium chloride or by the reduction of a mixture of barium oxide and barium peroxide by means of aluminum in a special type of vacuum furnace which is electrically heated.

11. Beryllium and Its Uses

This metal is very hard and has a bright, shiny luster. It is difficult to produce, expensive (about \$15 per pound), and is used only to a limited extent, largely in the production of a few alloys to which it adds lightness, hardness, and strength. An alloy with copper containing about two per cent of beryllium (page 655) is perhaps the best known and most widely used of the beryllium alloys. This alloy, when cooled rapidly, is a soft, solid solution of beryllium in copper. It becomes harder and stronger when heated for some time to a temperature of 400° to 500°. During this heat treatment some of the beryllium separates from the solid solution as crystals of very small size dispersed throughout the copper. This alloy is very

resistant to corrosion and is used to make springs of remarkable resiliency and resistance to fatigue. Copper-beryllium and nickel-beryllium alloys are used to make some of the parts of airplane motors.

12. Properties and Uses of Magnesium

Magnesium has a density of 1.74 and is like silver in appearance. It does not react very readily with oxygen at low temperatures because of the formation of a thin coating of oxide or basic carbonate on the surface. This coat protects the metal from further oxidation. It is used in the manufacturing of signal flares and flashlight powders, to remove gases from radio tubes, to deoxidize and to remove nitrogen and sulfur from certain metals, such as copper, and nickel alloys, and in the production of various magnesium alloys. Added to aluminum it forms the alloys called *magnalium* and *duralumin*, which are light and possess high tensile strength. *Dow metal* is also an alloy of similar properties, it contains aluminum, zinc, and approximately 90 per cent of magnesium. It can be cast, forged, pressed, rolled, and drawn, and hence it can be produced and used in almost any form, including plates, rods, and tubes. Such metals as these alloys are now widely used in airplane construction, in the pistons of motors, and elsewhere to secure lightness without loss of strength in bulky structures and devices, such as trucks and railway cars. Commercially, magnesium is by far the most important of the metals of this family. The producing capacity of the United States during World War II has been estimated as about 725,000,000 pounds per annum.

13. Properties and Uses of Barium, Calcium, and Strontium

Metallic barium is used to remove gases in the manufacture of radio tubes and to remove oxygen in the refining of copper. An alloy of barium and nickel is used to make the points of spark plugs, barium is useful for this purpose because of the ease with

which it emits electrons when it is heated. One of the most important alloys of barium is *Frary metal*, which contains lead, barium, and calcium. This alloy is used as a bearing metal. Barium is a silvery white metal. It is almost as soft as lead. It combines readily with oxygen, even igniting spontaneously in moist air. It is much more active than beryllium, magnesium, and calcium and slightly more active than strontium.

Calcium is a white, silvery metal when freshly prepared, but it combines readily with both oxygen and nitrogen and tarnishes to produce a gray and slightly yellow surface. It tends to have a crystalline structure, and is much harder than barium. It is, however, malleable and ductile. Its use in preparing bearing metals has been suggested above (*Frary metal*). Because of its tendency to react with water, the metal is sometimes used in drying organic liquids, such as alcohol. It is an excellent reducing agent and would undoubtedly be used in this capacity in reducing the oxides of other metals and other substances, in the place of metallic sodium, if it could be produced at a more reasonable cost. It is used to produce certain metals such as chromium, thorium, and cesium by reduction of their compounds. It has also been used in deep-sea sounding devices, in which its use depends upon the reaction of the metal with water to liberate hydrogen. In recent years, several new uses for calcium have been introduced. Small amounts have been found to be of value in the lead used in storage batteries, it is used in the production of steel, nickel, magnesium, aluminum, and other metals, in the purification of lead, and for other purposes.

Strontium has the same general properties as calcium and can be produced by similar methods, because it is not abundant and therefore is costly to produce, it has no commercial uses.

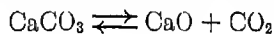
COMPOUNDS OF CALCIUM

Although magnesium is the most important *metal* of the group, the *compounds* of

calcium rank first. This element has many compounds that occur naturally, the most important of which are limestone and dolomite, phosphorite, gypsum, and fluor spar. Most of the compounds of calcium that are manufactured are made from the carbonate (limestone). This substance reacts readily with acids to form salts because of the liberation of carbon dioxide. The salts produced are purified by repeated crystallizations. The carbonate decomposes readily when it is heated, liberating carbon dioxide and forming the oxide, which is an important commercial substance itself and also serves as the starting material in the manufacture of other calcium compounds.

14 Calcium Oxide (CaO)

This is the substance commonly called *quicklime*. It can be produced by heating the metal in the air, but this process is, of course, impractical because of the cost of preparing the metal. It is produced commercially by the calcination of limestone.



Since this reaction is reversible, the carbon dioxide must be removed rapidly in order that the decomposition of the limestone may be complete. If the reaction occurs in a closed vessel, equilibrium is reached as soon as the pressure of the carbon dioxide in the closed space becomes equal to the *dissociation pressure* of the calcium carbonate. In order to avoid the production of equilibrium, the reaction is carried out in a continuous current of air, which sweeps the carbon dioxide away from the solid materials as rapidly as it is formed. Furthermore, if the reaction is carried out at 900°, or at a higher temperature, the dissociation pressure is greater than the pressure of the air with which the carbon dioxide mixes, hence there is no chance, at this temperature, that the carbon dioxide can collect in sufficient quantity to produce a pressure that exceeds the dissociation pressure.

Lime is made commercially in kilns, which

are large chimney-like furnaces about 60 feet in height and 10–15 feet in diameter. They may be either “straight up and down,” or they may have a bowl two thirds of the way down with tapering walls both above and below. Limestone is dumped in at the top, and the lime is drawn off into cars at the bottom. Heat for the calcination is supplied by fire boxes near the bottom. These open directly into the kiln and provide a draft, which draws in air at the bottom of the kiln to aid in removing the carbon dioxide. At one time, the long flames of wood fires were thought to be necessary in making lime, but now coal is usually the fuel employed in the lime kiln, and gas is sometimes used. The temperature at which the carbonate is decomposed is around 1000°C . Very high temperatures produce “dead-burned” lime, which is relatively inert, probably because of the fusion of the silicates contained in the stone or made by the reaction of the lime with silica. Lime is also produced in rotary kilns, similar to those used in the cement industry (page 664). Powdered coal or gas is used as fuel in these kilns.

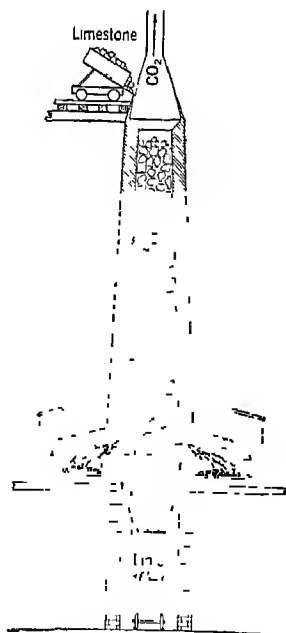
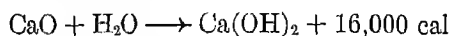


Figure 301 Lime Kiln

Commercial lime may be slightly brown or yellow in color due to the presence of iron compounds and other substances. The pure oxide is white. It melts at about 2570° and boils at 2850° . When heated to a high temperature, such as that of the oxy-hydrogen blow pipe, it emits an intense light, called “lime-light.” Freshly prepared lime reacts vigorously with water to form the hydroxide and to liberate heat in large quantities. This reaction is called “slaking,” and in commercial practice the hydroxide is called “slaked lime” or “hydrated” lime. It is not, of course, a hydrate.



Since it combines readily with water, calcium oxide is often used as a drying agent for such substances as alcohol and ammonia. Mixed with sodium hydroxide (solid) it forms “soda-lime,” which is used to dry gases and at the same time to remove carbon dioxide from them. When “quicklime” is left exposed to the air for some time, it becomes “air-slaked.” This means that it absorbs water from the air to form the hydroxide. At the same time it also absorbs some carbon dioxide to form calcium carbonate. “Air-slaked” lime is practically worthless.

The normal annual production of lime in the United States is about 4,000,000 tons. Because of the abundant deposits of limestone it can be produced in almost all parts of the country. Those limestones which contain more than four or five per cent of magnesium carbonate produce limes which hydrate slowly and are not so desirable for some purposes as lime made from more nearly pure calcium carbonate. The limes containing magnesium oxide, and particularly some of those produced from dolomites, are, however, more satisfactory for some purposes than the high calcium limes. This is true, for example, in the manufacture of the “slaked” lime that is used on walls as the finishing coat of plaster.

Other uses of lime include the following as a flux in the smelting of many ores of the

metals, in the manufacture of glass, as a polishing powder (Vienna lime), and in the production of calcium carbide, calcium cyanamide, etc

15. Calcium Hydroxide, $\text{Ca}(\text{OH})_2$

The preparation of this substance from calcium oxide has been described in the preceding section. If heated to 450° – 500° , the hydroxide decomposes into water and calcium oxide. Calcium hydroxide is a white, powdery substance. Contrary to the general rule, its solubility in water increases as the temperature decreases.

SOLUBILITY OF CALCIUM HYDROXIDE

(in 1000 ml. of water)	
10°	1.76 g
20°	1.65 g
50°	1.28 g
100°	0.8 g

Calcium hydroxide has many uses. It is a moderately strong base, and because of its low cost it is often used when a base is required. For this purpose a solution in water (limewater), or a suspension of the solid in water, can be employed. The following are some of its most important commercial applications: the production of ammonia, sodium hydroxide, bleaching powder, and insecticides, such as lime-sulfur sprays, the treatment of acid soils, the removal of hair from hides in making leather, the softening of water, the production of mortar, plaster, stucco, and similar structural materials, and the manufacture of paper, glass, cement, and whitewash.

16. Mortar

This material is made by mixing about one part of calcium hydroxide (slaked lime) with three parts of sand and adding enough water to make a thick, pasty mass. The hardening of mortar involves several changes: (1) the water evaporates, (2) carbon dioxide is absorbed from the air and forms calcium carbonate, (3) there is also a slow reaction that forms calcium silicate. The sand makes the mortar more porous and prevents undue shrinkage upon drying. Mortar may also

contain cement. It is used to hold in place various structural materials, such as stone, brick, tile, and concrete blocks.

Plaster. At one time the interior walls of buildings were covered with plaster made from calcium hydroxide, sand, and hair, with a "finish coat" of pure slaked lime. Most of the plaster used today is composed principally of plaster of Paris ($2\text{CaSO}_4\cdot\text{H}_2\text{O}$). **Stucco** is plaster which is used to cover the outside walls of buildings. It is composed of sand and a mixture of lime and cement to bind the grains of sand together. Stucco has been used for about 5000 years. Until the use of cement was developed, it consisted of a mixture of sand and lime.

17. Calcium Carbonate (CaCO_3)

This is the most abundant calcium compound found naturally. It has two crystalline forms, both of which are found in the earth. *Calcite*, the more stable of the two forms, crystallizes in the hexagonal system. *Aragonite* crystallizes in the rhombic system. Upon heating, the latter changes into the former, but at ordinary temperature the change is very slow.

The most familiar form of calcium carbonate is limestone. This occurs as stratified layers of rock, which have been formed by the deposition of calcium carbonate on the floors of seas. Subsequent geological changes have elevated the deposits above the surface of the water and have converted them into hard masses. Other deposits of sandstone and shale may later have been deposited upon the limestone, which is often found below strata of these rocks. Limestone is never pure calcium carbonate. Its color may be white, yellow, brown, blue, gray, or black because of impurities. Almost all limestones contain some magnesium carbonate, clay, sand, and compounds of iron and aluminum. Some contain considerable quantities of organic material. The fossil remains of various shell-creatures of the seas in which the deposit was formed are very often found in the rock.

Other natural forms of calcium carbonate are *chalk*, *marl*, a mixture of calcium carbon-

ate and clay, *Iceland spar*, which is practically pure calcite, *marble*, which has been made from limestone under the influence of heat and high pressures, and which is composed of small crystals of calcite, *pearls*, *coral*, *shells*, *stalactites* and *stalagmites*, which are deposits formed upon the roofs or floors of caves by the water that seeps into the cave from above and which contains calcium carbonate in solution, and *aragonite*

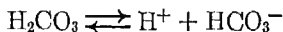
A large amount of the limestone quarried in the United States each year is used in building macadamized roads and concrete structures. Large quantities are also used as building stone. It is also used to neutralize the acids in soils, as a flux, and in the manufacture of glass, cement, lime, and many calcium compounds. *Whiting*, finely ground and carefully cleaned chalk, is used in polishes, pigments, and putty. Some dental powders and pastes contain *precipitated* chalk which is made by precipitating calcium carbonate from solutions containing the calcium ion

18. Calcium Bicarbonate, $\text{Ca}(\text{HCO}_3)_2$

Calcium carbonate is only slightly soluble in water. It dissolves much more readily in water that contains carbon dioxide in solution, because of the conversion of the insoluble normal carbonate into the more soluble acid carbonate



The carbonic acid of the solution ionizes slightly



Since the ionization constant of HCO_3^- is very small,

$$K_i = \frac{[\text{H}^+] \times [\text{CO}_3^{=}]}{[\text{HCO}_3^-]}$$

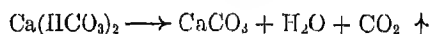
the addition of H^+ ions from the carbonic acid reduces the concentration of $\text{CO}_3^{=}$ ion, because the two ions combine to form the slightly ionized bicarbonate ion, HCO_3^- . The reduction in the concentration of the carbonate ion causes more calcium carbonate

to dissolve in an attempt to saturate the solution and to produce a product of the concentrations of Ca^{++} and $\text{CO}_3^{=}$ ions which is equal to the solubility product,

$$[\text{Ca}^{++}] \times [\text{CO}_3^{=}] = S P = 1 \times 10^{-8}$$

The water which falls as rain contains carbon dioxide, which is dissolved from the air. Surface waters also dissolve carbon dioxide from soils where it is produced by the slow oxidation and decay of organic materials. When these waters come into contact with limestone rocks in the earth, the stone disappears due to the reaction described above. This is an important factor in the formation of caves in limestone regions. If this water finds its way through the rocks into a cave, the water slowly evaporates, carbon dioxide is liberated, and calcium carbonate is deposited. If this deposit accumulates at a point on the cave's ceiling, where drops of solution seep through, the formation is called a *stalactite*. If it is built up by drops falling at some point on the floor, it is called a *stalagmite*.

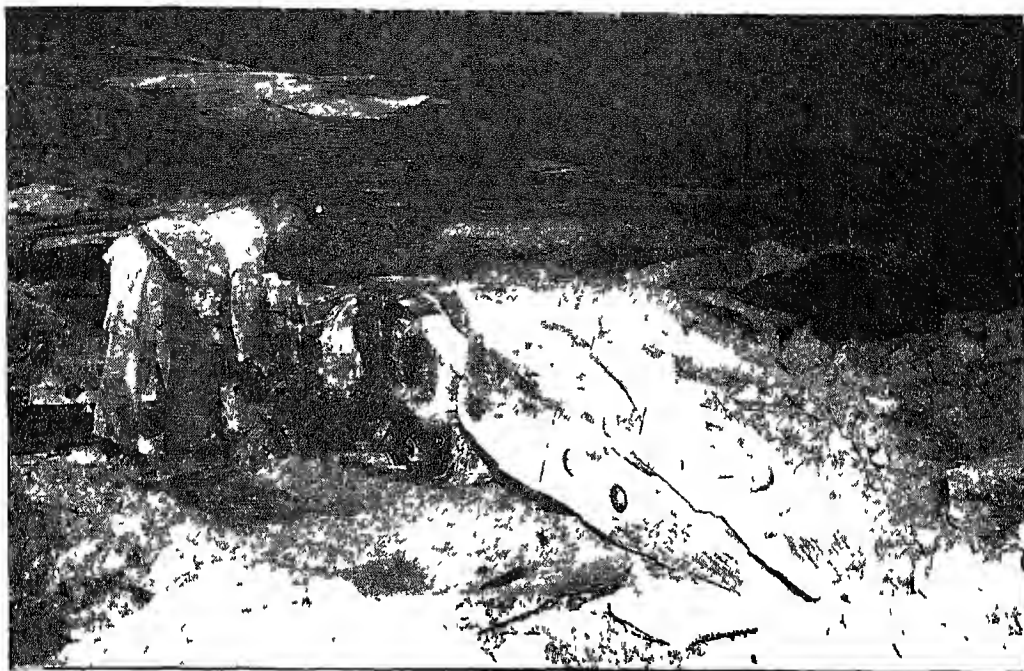
Calcium bicarbonate is converted very readily into the normal carbonate, when a solution in which it is dissolved is heated to boiling. The increase in temperature causes the carbon dioxide to be completely removed and reverses the reaction



If the water from springs and wells has been in contact with limestone in the earth, it contains calcium bicarbonate. This substance forms a deposit of calcium carbonate when the water is heated in kettles or boilers. Such waters are undesirable for use in boilers, unless some means of preventing the formation of "boiler-scale" is employed.

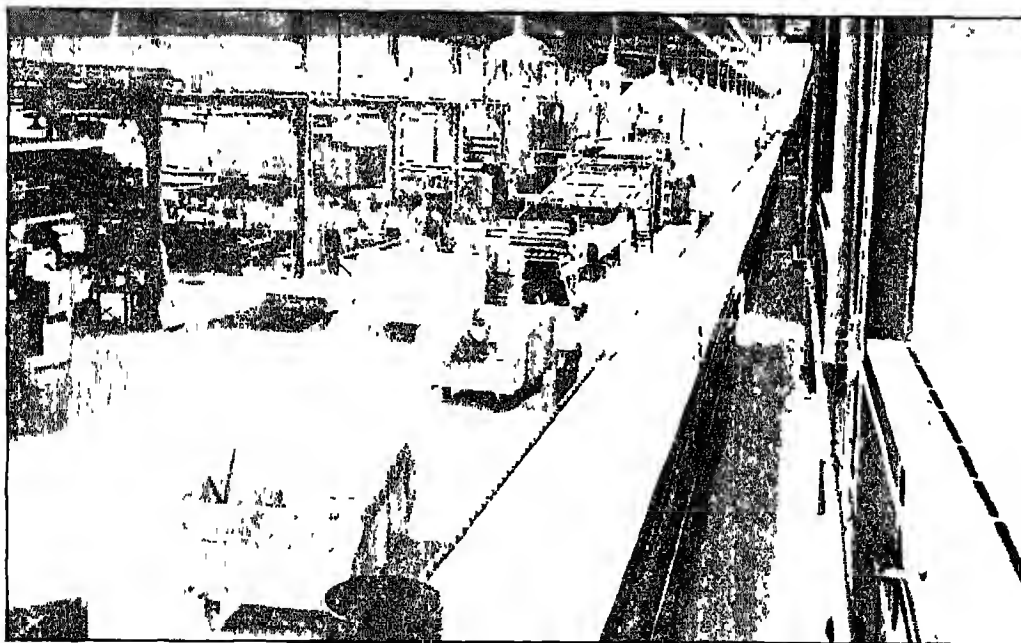
19 Calcium Chloride

Although calcium chloride can be produced very readily, by treating lime, calcium hydroxide, or calcium carbonate with hydrochloric acid, it is usually obtained as a by-product of the Solvay process for producing sodium carbonate and as a by-product of other industries. This substance forms two hydrates $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot \text{H}_2\text{O}$. The hexahydrate crystallizes from aqueous solutions. When heated, this hydrate forms the



Courtesy of National Gypsum Company

Figure 302 Mining Rock Gypsum

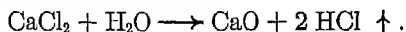


Courtesy of National Gypsum Company

Figure 303. General View of a Plaster Board Plant

Showing an unbroken stream of plaster wallboard moving along a conveyor belt to be dried, cut into panels, packed, and shipped

monohydrate. The latter is a porous substance which is very deliquescent. It is often used as a drying agent for gases and organic liquids because it combines with water to form the hexahydrate. When heated to a higher temperature, the monohydrate is changed to the anhydrous salt. During dehydration, some calcium oxide is produced by hydrolysis



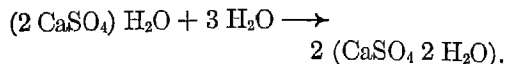
The oxide causes the anhydrous salt, as it is usually prepared, to have an alkaline reaction

Calcium chloride is used to keep down the dust on highways. Owing to its deliquescence, the salt removes water from the air and forms a solution, which is very highly concentrated and which therefore has a very low aqueous vapor tension. It is also used in the manufacture of cement and in curing concrete, since it prevents such materials from drying out too quickly. A solution of calcium chloride in water serves as an excellent bime for use in cold storage and refrigerating plants. A mixture freezing as low as -55° can be prepared by dissolving the hexahydrate in water.

20. Calcium Sulfate (CaSO_4)

This substance occurs in nature as *gypsum*, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. The anhydrous form of calcium sulfate occurs as the mineral *anhydrite*. *Alabaster*, *satin spar*, and *selenite* are crystalline forms of the dihydrate. Gypsum occurs in extensive deposits in New York, Ohio, Iowa, Michigan, Texas, and Nevada. It is widely used, as shown by the annual production in the United States of more than 5,000,000 tons. Our common crayon (chalk) is made from it. It is also used in cement to retard the rate of setting, in certain fertilizers, in some paints, and in paper. Used in fertilizers, it aids by converting ammonium carbonate into ammonium sulfate. The latter ammonium salt is more stable than the former, and when it is produced, there is not so much loss of ammonia to the air.

Plaster of Paris is made by partially dehydrating gypsum at a temperature of about 125° . The product is $(2 \text{CaSO}_4) \cdot \text{H}_2\text{O}$. When this substance is mixed with water, the following reaction takes place



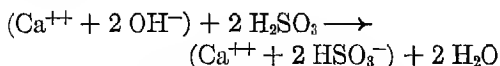
The dihydrate that is produced by this reaction forms a hard mass, which has the same composition as gypsum but differs in being more difficult to dehydrate. Because of its rapid rate of setting and its tendency to expand as it solidifies, plaster of Paris is used in making surgical casts, models, molds, and statuary. Its most important use is in the manufacture of plaster for covering the interior walls of buildings. These plasters also contain lime. Stucco may be made from plaster of Paris and glue, which acts as a binding agent.

Large quantities of gypsum and plaster of Paris are used in the building industry. The pulverized rock gypsum is heated to expel most of the water that it contains, then it is mixed with mineral wool, asbestos, sawdust, or other similar materials. The mixture is wet and molded into blocks, tile, lath, boards, and other building forms, which become hard as the calcium sulfate combines with the water to form the hydrate once again. *Wall board* is made from a mixture of plaster of Paris and wood pulp or by binding sheets of paper together with layers of plaster of Paris between them. Heating gypsum to 450° – 500° produces a very hard cement used to make flooring tile. *Keene's cement* is made by heating gypsum twice, after the first heating, the product is treated with a solution of alum, and it is then heated a second time. This cement is used as a very hard finish plaster. Anhydrous calcium sulfate is used as a drying agent.

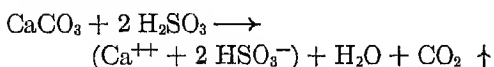
21. Calcium Sulfite and Bisulfite

Normal calcium sulfite, CaSO_3 , is only slightly soluble and is produced as a white precipitate when a solution of any soluble sulfite is mixed with a solution containing calcium ion. Like the normal carbonate, it is converted into the acid salt

when it is treated with a solution of the acid, which in this case is formed by dissolving sulfur dioxide in water. The acid sulfite or bisulfite, $\text{Ca}(\text{HSO}_3)_2$, is soluble. It is prepared by titrating a suspension of calcium hydroxide in water with sulfur dioxide.



It is also made by passing sulfur dioxide over wet limestone.



Calcium bisulfite is used extensively in the manufacture of paper (page 603).

22. Other Compounds of Calcium

The carbide, cyanamide, and phosphates of calcium have been discussed elsewhere in this book. Other important compounds of this element include the nitrate, $\text{Ca}(\text{NO}_3)_2$, which is used as a fertilizer; calcium hypochlorite and bleaching powder; calcium acetate, from which acetone is prepared; calcium chlorate, $\text{Ca}(\text{ClO}_3)_2$, which is used to kill weeds; calcium oxalate, CaC_2O_4 (page 587); calcium sulfide, CaS , and persulfides, such as CaS_4 ; calcium silicate, CaSiO_3 , which is the mineral known as wollastonite; calcium tungstate, CaWO_4 , which is used in making luminous paint; calcium borates, which are found in California and from which borax may be made (page 539); and calcium fluoride (page 342).

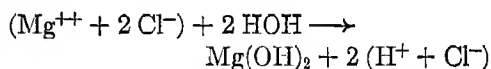
23. Hard Water

Although the bicarbonate of calcium is the most common substance found in "hard" water, it is not the only substance present in such waters. Magnesium bicarbonate, produced in the same manner as calcium bicarbonate, causes similar losses of soap in the laundry (page 176) and produces scale when the water in which it is dissolved is used to generate steam in boilers. Both of these substances produce *temporary hardness* of water, so called because the hardness may be overcome by boiling the water. In boiling water the bicarbonates are converted into

normal carbonates, which are only slightly soluble, and, as these precipitate, the magnesium and calcium ions are removed from the solution.

Whenever water in the earth comes in contact with gypsum, this substance dissolves slightly. Calcium sulfate, together with smaller amounts of other salts, such as magnesium sulfate and the chlorides of calcium and magnesium, are responsible for the condition called *permanent hardness* of water. The metallic ions of permanently hard water cannot be removed by boiling, and to soften such water substances must be added to convert calcium and magnesium ions into slightly soluble compounds that will precipitate.

The substances largely responsible for the hardness of water are, therefore, the bicarbonates, sulfates, and chlorides of calcium and magnesium, and, sometimes, corresponding compounds of iron; only the metallic ions of these compounds are involved in the failure of soap to lather in hard water. Magnesium chloride is objectionable in water used in boilers because of its hydrolysis.

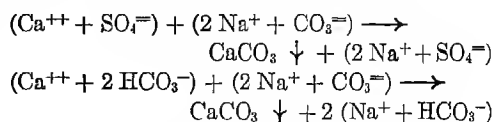


The acid formed by this reaction causes corrosion of the boilers.

24. Water Softeners

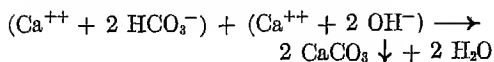
The following materials are examples of substances widely used to soften water by precipitation methods.

(1) *Sodium Carbonate*. This substance converts the ions of calcium and magnesium into the insoluble normal carbonate and relieves, therefore, both temporary and permanent hardness.

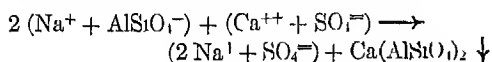


(2) *Calcium Hydroxide*. A suspension of milk of lime converts the bicarbonate into the

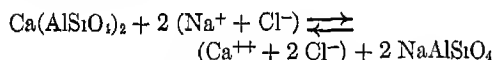
normal carbonate but has little or no effect upon calcium sulfate. It also converts soluble magnesium salts, such as the chloride or sulfate, into the insoluble hydroxide



(3) *Zeolites and Permutit* The zeolites (page 534) are naturally occurring sodium aluminum silicates, $\text{NaAlSi}_3\text{O}_8$. Permutit is a manufactured product of about the same nature. When water containing calcium or magnesium ions in solution passes slowly through rather thick layers of this material, the sodium in the zeolite is replaced by calcium, and the water is freed of the latter



This process of water softening can be operated continuously, since the calcium aluminum silicate can be reconverted into the sodium compound by treating the zeolite, after it has been used for some time, with a concentrated solution of sodium chloride



The reversal of the reaction depends upon the increase in the concentration of the sodium ion. The material that has been thoroughly washed with brine is washed with pure water and is then ready to be used over again in softening more water. This softening process is used in laundries and in homes where the water is too hard to be used without great waste of soap and the undesirable effects accompanying the formation of calcium and magnesium soaps as deposits upon clothing. It relieves both permanent and temporary hardness.

(4) *Other Precipitating Reagents* Other substances used to form insoluble salts of calcium, and in some cases insoluble magnesium salts also, include borax, trisodium phosphate, and ammonium hydroxide. Borax and ammonium hydroxide are effective in relieving temporary hardness because of the alkaline character of their solutions. Trisodium phosphate precipitates calcium and magnesium as insoluble phosphates and also produces an alkaline solution, which converts the bicarbonate into the normal salt. The alkaline solutions of sodium phosphate and borax are produced by the hydrolysis of these salts

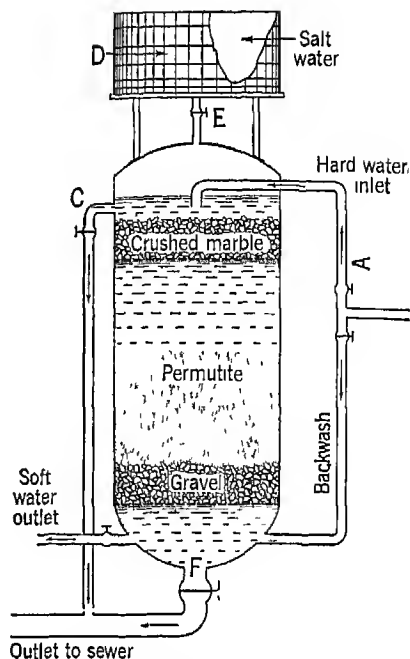


Figure 304 The Permutit Water Softener

The water to be treated enters through A. Brine for the regeneration of the permutit is stored in D, flows into the permutit chamber through E, and out as waste through F.

25 How the Hardness of Water is Expressed

When water is analyzed to determine its hardness, the results are usually expressed as parts of calcium carbonate per million. All substances producing hardness are represented in terms of equivalent amounts of calcium carbonate. Sometimes the results are expressed in degrees, one degree representing one grain per gallon, or 17.1 parts per million.

CEMENT

There are several varieties of *cement*. In general, the term is applied to materials that can be made up as pastes by mixing them with water and which harden or "set" in water as well as in air. When we think of cement, however, we have in mind, usually, the material known as *Portland cement*. The name is derived from the name of an English town, Portland. Since about 1900, its use has grown until it is now one of the

most important of structural materials. *Concrete* is the name applied to the hardened mass that results when a mixture of sand, crushed stone, cement, and water is poured into "forms" and allowed to stand. If steel wire, cables, or rods are placed in the mixture and allowed to become embedded in the solid structure, reinforced concrete is produced.

Portland cement is produced from a mixture of limestone or marl and clay or shale. These substances are finely ground and mixed, and the mixture is heated or "burned" in a rotary kiln (Figure 305). At the lower end of the kiln, heat is supplied by burning gas or powdered coal, and the ground raw materials are fed in from a hopper at the upper end. The material slowly moves down through the kiln, which is inclined, and at the lower end is heated to a temperature of about 1500° . The powdered materials are partially fused and pass out of the lower end of the kiln in the form of small lumps, known as *clinker*. The material is then cooled, and finally is ground to a powder. About three per cent of gypsum is ground with it to retard the rate of setting. Unless some retarding agent such as calcium sulfate is used, the cement may harden before it can be placed in the position where it is to be used.

During the formation of the clinker certain chemical reactions occur. These produce, essentially, tricalcium silicate, $\text{Ca}_3\text{SiO}_5(3\text{CaO}\cdot\text{SiO}_2)$, dicalcium silicate, $\text{Ca}_2\text{SiO}_4(2\text{CaO}\cdot\text{SiO}_2)$, and cal-

cium aluminate, $\text{Ca}_3(\text{AlO}_3)_2(3\text{CaO}\cdot\text{Al}_2\text{O}_3)$. The reactions which occur during the hardening of cement are very complex and not completely understood. Two kinds of reactions, however, are known to occur: hydration and hydrolysis. The hydration of the compounds present in cement produces crystals. Hydrolysis of calcium silicate and calcium aluminate produces gelatinous compounds, such as silicic acid and aluminum hydroxide, which gradually harden and hold the crystals tightly cemented together. Since all of the substances which result as the cement sets are insoluble in water, cement will harden in water, although the set occurs best in the air. The process continues for several weeks after an initial period of rapid hardening during the first thirty hours.

The normal annual production of Portland cement in the United States is approximately 165,000,000 barrels. Table 41 shows its average composition, each constituent being represented as the oxide.

TABLE 41
Composition of Portland Cement

Constituent	Average percentage
Silica, SiO_2	22.5
Alumina, Al_2O_3	7.5
Ferric oxide, Fe_2O_3	3.5
Lime, CaO	62.5
Magnesia, MgO	2.5
Oxides of Sodium and Potassium (Na_2O and K_2O)	1.5

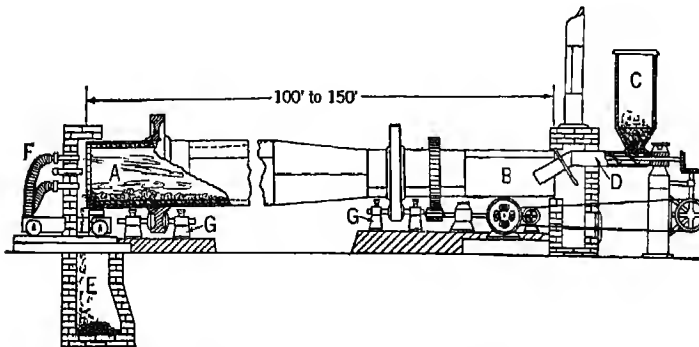


Figure 305 Cement Kiln

The raw materials are fed into the kiln (B) from the hopper (C). Powdered coal and air are blown into the lower end of the kiln through F. Clinker falls out of the kiln at A into the receiver E. The kiln is rotated by means of the gears G.

If gypsum is added, the cement's composition also shows about two per cent of sulfur trioxide, SO_3 , and a correspondingly larger percentage of lime and somewhat smaller percentages of the other constituents

26. Other Cements

A rapidly setting cement is made by fusing a mixture of finely ground limestone and the mineral bauxite, which is the oxide of aluminum. This cement is composed, therefore, of calcium aluminate. *Keene's cement* may be produced by heating gypsum that has been treated with a solution of alum (potassium aluminum sulfate). Plumbers use a cement made from a mixture of glycerine and litharge, PbO . Zinc oxide and phosphoric acid form one of the common cements used in dentistry. Solutions of pyroxylin in amyl acetate, or other solvents, may be used to cement wood, glass, and porcelain. A solution of sodium silicate is used to cement pasteboard in making cartons. Tricalcium silicate is used as a quick-setting cement. Also see Sorel cement, page 667

COMPOUNDS OF MAGNESIUM

Most of the compounds of magnesium are produced either from the carbonate, which is found in nature as the mineral magnesite (page 654), or from magnesium chloride which is recovered during the production of potassium salts from the Stassfurt deposits, from the liquor remaining after salt is crystallized from brines pumped from salt wells, or from sea water.

27. Magnesium Oxide and Magnesium Hydroxide

The oxide of magnesium is sometimes called *magnesia*. It can be produced by allowing the metal to burn in the air or by the decomposition of the carbonate. The latter method is most often used, since the carbonate decomposes very readily upon heating, more readily in fact than calcium carbonate. The oxide reacts with water less

rapidly and less vigorously than the oxide of calcium, which it resembles in general properties. It has a melting point of about 2800° , and because of this property is used in making fire brick and crucibles, and as a lining of furnaces. It also finds some use in the manufacture of certain kinds of stucco, cement, and building materials. Magnesia produced by heating magnesite at a temperature of about 1400° is inactive and a very poor conductor of heat, it is used as a heat insulator in covering hot water and steam pipes.

The hydroxide is less soluble and less basic in character than calcium hydroxide. It is formed as a precipitate when a soluble hydroxide is added to a solution containing magnesium ion. The precipitate can be made to dissolve by adding ammonium salts. This effect is due to the tendency of the ammonium ion to react with the hydroxyl ion to form ammonia and water. If a very great concentration of ammonium ion is present, the concentration of the hydroxyl ion is reduced to a small value. Since the product of the concentration of the magnesium ion and the square of the concentration of the hydroxyl ion is a constant, in a saturated solution of $\text{Mg}(\text{OH})_2$, the reduction in the concentration of the OH^- ion calls for a corresponding increase in the concentration of the Mg^{++} ion. This requirement means that more and more of the precipitate of magnesium hydroxide must dissolve as the concentration of the OH^- ion is reduced. If this concentration is reduced sufficiently, all of the precipitate may be made to dissolve.

$$[\text{Mg}^{++}] \times [\text{OH}^-]^2 = \text{solubility product} = 1 \times 10^{-11}$$

Milk of magnesia is the name given to a suspension of the hydroxide in water. This suspension is used in medicine as a laxative and as an anti-acid. It is also used as an antidote when strong acids are swallowed. The magnesium ion is not injurious to the body, and the concentration of the hydroxyl ion in the suspension is so small that there is no danger.

28. Magnesium Carbonate

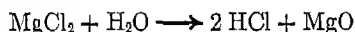
Like calcium, magnesium forms a slightly soluble normal carbonate and a soluble bicarbonate, $\text{Mg}(\text{HCO}_3)_2$. The normal carbonate is

more soluble, however, than normal calcium carbonate. The addition of a solution of sodium carbonate to a solution containing magnesium ion forms a precipitate of the basic carbonate, $(3 \text{MgCO}_3) \cdot \text{Mg}(\text{OH})_2 \cdot 4 \text{H}_2\text{O}$, sometimes called *magnesia alba*, which is used in dental powders and pastes, in polishing powders, and as a heat insulator.

29. Other Salts of Magnesium

Magnesium sulfate occurs naturally as *kieserite*, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, and *epsomite*, $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$. The latter, in a pure form, is familiar as *Epsom salts*. It is also found in many mineral waters, in salt deposits, and in the mother liquor after salt is removed from sea water or from the brines of salt wells. It is used in medicine as a purgative, in weighting cotton and silk, in sizing paper, and in fireproofing fabric.

Magnesium chloride is found in sea water and in salt deposits. One of its most important natural occurrences is as the double salt, *carnallite* ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6 \text{H}_2\text{O}$), of the Stassfurt salts, from which it may be obtained as a by-product of the recovery of the potassium chloride. Magnesium chloride crystallizes from aqueous solutions as the hexahydrate, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. Upon heating, this hydrate does not form the anhydrous salt but reacts to form hydrochloric acid and magnesium oxide.



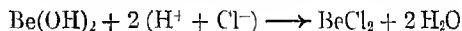
This reaction has been suggested as a means of producing hydrochloric acid. Magnesium oxide and magnesium chloride react to form the basic salt, $\text{MgO} \cdot \text{MgCl}_2$. The formation of this compound is the essential principle of *Sorel cement*, which is used to produce a substitute for tile in covering walls and floors. When it contains small amounts of magnesium chloride, salt becomes moist and clogs the openings of the salt "shaker." This condition is caused by the deliquescence of the magnesium chloride and can be prevented by adding starch to keep the salt from "caking," or by adding sodium bicarbonate, which precipitates the magnesium as the basic carbonate, $\text{Mg}(\text{OH})_2 \cdot 3 \text{MgCO}_3 \cdot 4 \text{H}_2\text{O}$.

Ammonium magnesium phosphate, NH_4MgPO_4 , a slightly soluble crystalline solid, is formed whenever a soluble phosphate is added to a solution containing magnesium and ammonium ions. The formation of this compound is a means of detect-

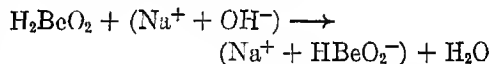
ing the presence of magnesium ion or phosphate ion in a solution. The same substance is formed in the quantitative determination of either of these ions in a solution. In this determination the ammonium magnesium phosphate is precipitated by adding ammonium hydroxide and sodium phosphate, if magnesium is to be determined, or by adding magnesium chloride, if the phosphate ion is to be determined. The precipitate is filtered and ignited, whereupon it is converted into the pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, which is weighed.

COMPOUNDS OF BERYLLIUM

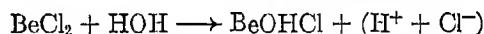
Beryllium hydroxide is amphoteric. It dissolves in solutions of acids to form salts in which beryllium acts as a divalent metal.



It also dissolves in solutions of bases to form salts, called *beryllates*, in which beryllium forms the divalent negative ion, BeO_2^{2-} or the univalent ion HBeO_2^- .



Beryllium chloride is highly hydrolyzed.



This behavior is in keeping, of course, with the weak basic character of beryllium hydroxide, for, as we have frequently observed, the tendency of the salts of a metal to hydrolyze increases as the amphoteric or non-metallic character of the element becomes more pronounced. Other salts of beryllium, such as the sulfate, BeSO_4 , and a basic carbonate are also known, but none of these compounds is important.

COMPOUNDS OF STRONTIUM

Strontium compounds are less abundant than those of magnesium, calcium, and barium. The element resembles calcium, and its compounds have properties that are intermediate between those of the corresponding compounds of calcium and barium.

Strontium hydroxide is a moderately strong base and dissolves to a considerable extent in hot water. It is sometimes used in sugar refineries in some parts of the world to remove cane sugar from molasses. With sucrose, strontium hydroxide forms an insoluble compound that can be separated by filtration from the invert sugar and other non-crystallizing sugars of molasses. The precipitate is mixed with water and then treated with carbon dioxide, which precipitates strontium as the carbonate and liberates free, pure sucrose.

A few compounds of strontium, including the bromide and iodide, are used in medicine. The most important use of strontium compounds is in fireworks, flares, fuses, and other lights, to which the strontium gives a red color. Strontium nitrate is most often used for this purpose.

The separation of calcium and strontium in analytical chemistry is difficult because their compounds dissolve in water to about the same extent. The most widely used method involves the precipitation of strontium as the sulfate, calcium sulfate being much more soluble than strontium sulfate. If a saturated solution of calcium sulfate is added to a solution containing Sr^{++} and Ca^{++} , there is, of course, little probability that CaSO_4 will be precipitated, since it is a solution of that substance that is added. This solution contains a sufficient concentration of SO_4^{--} ions to exceed the solubility product of SrSO_4 , even in solutions containing only a small concentration of Sr^{++} ion.

$$\begin{aligned} [\text{Sr}^{++}] \times [\text{SO}_4^{--}] &= 2.8 \times 10^{-7} = \text{S.P.} \\ [\text{Ca}^{++}] \times [\text{SO}_4^{--}] &= 6 \times 10^{-6} = \text{S.P.} \end{aligned}$$

COMPOUNDS OF BARIUM

30. Barium Oxide, Peroxide, and Hydroxide

The oxide of barium may be prepared by decomposing the carbonate, which occurs in nature as the mineral *witherite*. This decomposition is much more difficult to effect than the decomposition of calcium carbonate. A

temperature of approximately 1400° must be used to produce the oxide rapidly.



The reaction can be carried out at lower temperatures, by mixing finely divided carbon with the barium carbonate before it is heated. The carbon aids the reaction by converting the carbon dioxide as it is liberated into carbon monoxide and thus shifting the point of equilibrium of the reaction toward the right.

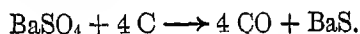
When heated at 500° – 600° in a current of air, barium oxide combines with oxygen to form *barium peroxide*, BaO_2 . If the barium peroxide is then heated to 700° – 800° , the reaction is reversed, and pure oxygen is liberated. This is the basis of Bunsen's process for producing oxygen (page 67). Barium peroxide may also be used to produce hydrogen peroxide (page 186).

Like quicklime, the oxide of barium is "slaked" by the addition of water. The hydroxide, $\text{Ba}(\text{OH})_2$, is formed. The oxide reacts with water vigorously and might be used to a greater extent as a dehydrating agent if it were more easily produced, and if barium compounds were as abundant as those of calcium. The hydroxide may also be produced by treating barium carbonate with superheated steam. It dissolves to a greater extent (37 g. per liter at 18°) in water than the hydroxides of the other alkaline earth metals, and the solution (0.1N) is ionized to the extent of 77 per cent of the hydroxide. It is therefore a moderately strong base. The solution, which is called *baryta water*, is used in certain analytical procedures in the chemical laboratory. When so used, it must be carefully stored out of contact with air in order that it may not absorb carbon dioxide, which reacts with the hydroxide to form the insoluble barium carbonate. Since the carbonate is precipitated, when it forms, a solution of barium hydroxide has this advantage over one of sodium or potassium hydroxide, which also absorbs carbon dioxide from the air. In solutions of

the alkali hydroxides, soluble carbonates are produced, and these give trouble in the titration of solutions with acids by interfering with the sharpness of the end point obtainable with an indicator. This trouble is not encountered in the use of the barium hydroxide solution since any carbonate that forms does not remain in solution.

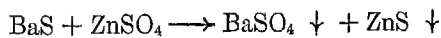
31 Barium Sulfate and Barium Sulfide

Since barium sulfate is the mineral in which barium occurs most abundantly, it is frequently used to produce other barium compounds. The sulfate is only slightly soluble even in acids. To convert it into the chloride or nitrate of barium, the sulfate must first be changed into a compound that will dissolve in solutions of HCl or HNO₃. The sulfate is first fused with sodium carbonate (page 651) to form barium carbonate, or it is reduced, by heating it with carbon, to barium sulfide.



The carbonate or the sulfide is then dissolved in hydrochloric or nitric acid to produce the chloride or nitrate of barium. These salts are then crystallized by the evaporation of the water from the solution.

Barium sulfide reacts with zinc sulfate to form barium sulfate and zinc sulfide, both of which are slightly soluble salts.



This reaction is the basis of the production of *lithopone*, a mixture of BaSO₄ and ZnS, which is used in paint. In addition to possessing excellent "covering power," lithopone has certain other advantages over white lead in paint. It is not poisonous, and it is not blackened by hydrogen sulfide, which converts the white lead of "lead" paints into black lead sulfide. It is used chiefly, however, in paints for interiors, since it slowly darkens when exposed for a long time to bright sunlight. The production of lithopone accounts for about one half of the

300,000 tons or more of barium products consumed in this country annually.

Barium sulfate itself is used in the manufacture of white paints as *permanent white*. Because of its tendency to form crystals, however, it does not possess satisfactory covering power, unless it is very finely divided. Barium sulfate is also used as a filler in rubber, oilcloth, linoleum, and paper. Paper "filled" with this salt is relatively heavy. Barium sulfate is also produced in the detection and quantitative estimation of either barium or sulfate ions. Because it is only very slightly soluble in water, the barium sulfate produced when barium chloride or nitrate is added to a solution containing a soluble sulfate, or when sodium or ammonium sulfate is added to a solution containing barium ion, may be separated by filtration, dried, and weighed as a quantitative measure of the quantity of sulfate ion or barium ion in the sample. Barium sulfate is used in securing X-ray photographs of the intestinal tract. This substance is opaque to X-rays, and the patient drinks a mixture of barium sulfate and water. Ground barite is placed in oil wells that produce natural gas; the barium sulfate sinks, forming a layer of heavy material at the bottom of the well and preventing the escape of the gas.

32 Other Salts of Barium

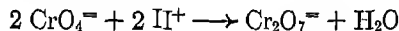
Certain other salts of barium have minor uses. The nitrate and chlorate are used to produce green colors in fireworks and signal lights of various kinds. The carbonate is used as a rat poison. The chloride is sometimes used to remove the sulfate which is present in sodium chloride as sodium or magnesium sulfate. Barium fluosilicate is used as an effective insecticide. Largely because of the wide use of lithopone, the production of barium compounds has become an important industry in the United States during the last quarter of a century. In a normal year the production of lithopone alone amounts to 150,000-200,000 tons.

33 Detection of Barium

In the presence of strontium ion barium

cannot be tested for successfully by adding a soluble sulfate to form barium sulfate. There is too much chance that strontium sulfate, which is also only slightly soluble, may precipitate. This difficulty may be avoided by using a saturated solution of strontium sulfate in the test for barium, since barium sulfate is less soluble than strontium sulfate.

Usually, the detection of barium depends upon the precipitation of barium as the chromate. In the separation of barium and strontium the chromate ion is preferable to the sulfate because there is a greater difference between the solubilities of the two chromates than there is between the solubilities of the two sulfates. The precipitation of strontium chromate may be avoided, and the detection of barium made still more positive, if the chromate ion is added to a solution acidified with acetic acid. The acid converts a portion of the chromate ions into the dichromate ions:



This reaction lessens the concentration of the chromate ion and renders less likely the chance that the solubility product of strontium chromate may be exceeded. The solubility product of barium chromate may be exceeded, even in the presence of a moderate concentration of the acid, since it is much smaller. To regulate the hydrogen ion concentration, and indirectly to regulate also the concentration of the chromate ion, sodium acetate is added along with the acetic acid. If this is not done, neither barium nor strontium chromate may be precipitated, unless a very limited and carefully determined amount of acid is added.

Review Exercises

1. From what mineral sources are the alkaline earth metals and their compounds produced?
2. In what way does the hydroxide of beryllium differ from the hydroxides of the other metals of this group?
3. Compare the solubilities of the oxalates, sul-

fates, chromates, and carbonates of calcium, strontium, and barium. (See Table of Solubility Products, Appendix.) How, in general, do the solubilities of the strontium compounds compare with those of calcium and barium?

4. If you were to attempt to precipitate only calcium from a solution containing the three chlorides, CaCl_2 , SrCl_2 , and BaCl_2 , which ion in the following list would you use? Chromate, oxalate, carbonate. Explain.
5. How would you convert the following substances one into another in the order indicated?
 - (a) $\text{CaCO}_3 \longrightarrow \text{CaO} \longrightarrow \text{Ca(OH)}_2 \longrightarrow \text{Ca(NO}_3)_2$
 - (b) $\text{Mg(HCO}_3)_2 \longrightarrow \text{MgCO}_3 \longrightarrow \text{MgCl}_2$
 - (c) $\text{BaSO}_4 \longrightarrow \text{Ba(NO}_3)_2 \longrightarrow \text{BaCO}_3 \longrightarrow \text{BaCl}_2$
6. Explain why ammonium salts interfere in the precipitation of magnesium hydroxide. Would you expect ammonium salts to have a similar effect upon the precipitation of the hydroxides of calcium, strontium, and barium? Explain.
7. Why is barium sulfate practically insoluble in strong acids, while barium carbonate and barium chromate, which have approximately the same or smaller solubilities in water than the sulfate, dissolve readily even in dilute HCl ?
8. The lime removed from a certain lime kiln during a day's run is 15 tons. Assuming that the rock is 95 per cent pure CaCO_3 and the remainder inert material, and that calcination is complete, what weight of stone is required to produce this quantity of lime and what (standard) volume of carbon dioxide is liberated?
9. Calculate the normality of saturated solutions of calcium hydroxide at 10° and 100° .
10. Assuming equal transportation costs, one ton of lime can be shipped for the same price as one ton of calcium hydroxide (slaked lime). What weight of calcium hydroxide could be produced from this weight of lime? What is the advantage of shipping slaked lime instead of quicklime?
11. The solubility of calcium sulfate is 0.2 g per 100 ml of water at 18°C . What weight of soap must be used to precipitate the calcium ion in 10 liters of water, if the water contains 20 per cent as much calcium sulfate as a sat-

- uated solution and if the soap is pure sodium palmitate?
12. What weight of barium sulfate is required to produce 1000 tons of lithopone?
 13. Compare the volumes of hydrogen produced, under the same conditions, by the reaction of HCl with 10 g each of calcium and magnesium.
 14. Why can barium sulfate be precipitated from a solution of barium chloride by adding a saturated solution of calcium sulfate, while calcium sulfate cannot be precipitated by adding a saturated solution of barium sulfate to a solution of calcium chloride?
 15. What effect does sodium acetate have upon the precipitation of barium chromate in a solution containing acetic acid, barium, and chromate, $\text{CrO}_4^{=}$, ions? Explain
 16. Enumerate as many uses as you can for limestone and lime in the manufacture of chemicals (One use for limestone, for example, is in the manufacture of calcium carbide)
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METALS OF THE B DIVISIONS OF GROUPS ONE AND TWO

TABLE 42
Properties of Copper, Silver, Gold, Zinc,
Cadmium, and Mercury

	At wt	Density	Melting point	Valences
Copper	63.57	8.9	1,083°	1, 2
Silver	107.88	10.5	960.5°	1
Gold	197.2	19.3	1,063°	1, 3
Mercury	200.61	13.546	-38.87°	1, 2
Zinc	65.38	7.14	419.4°	2

COPPER

1. History and Occurrence

Copper was probably the first metal to be widely used by man. Its name, originally *cyprium*, is derived from Cyprus, an island from which it was obtained by the Romans. Later it came to be called *cuprum*. Copper was obtained at Sinai at least 5000 years before the beginning of the Christian era, and many copper instruments and articles that are more than 6000 years old are in the possession of museums.

The most important deposit of *native* copper in the world is found in the Michigan peninsula in the region around Houghton. The ores of copper include oxides, sulfides, and carbonates. Probably the largest known deposit of copper is a sulfide which has been incompletely oxidized to the sulfate, this is in the Andes mountains of Chile. *Chalcopyrite*, CuFeS_2 , is one of the most valuable ores. Others are *chalcocite*, Cu_2S , *cuprite*, Cu_2O ; *melanconite*, CuO , and *malachite*, $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$. Almost all countries pro-

duce some copper. The extensive deposits of South America and Africa have, in recent years, become important sources of the metal, but at the present time the United States leads in production. The ores of the United States are found in Arizona, Utah, Montana, New Mexico, Tennessee, and California, in addition to the Michigan deposits of native copper to which we have previously referred. These states produce about one third of the world's annual copper production of 2,500,000 metric tons. Chile now ranks second to the United States, and Rhodesia, the Belgian Congo, and Canada also rank high in the production of copper.

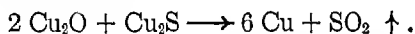
2 Metallurgy

The metallurgy of copper is a fairly simple process when the metal occurs in the uncombined state. The ore is ground and some of the gangue, or earthy material, is washed away by a stream of water. The material is then heated until the copper melts, and a flux is added to form a fusible slag with the gangue. The liquid slag rises to the top and the heavier copper collects on the bottom.

Ores that contain copper in the form of the oxide, hydroxide, or carbonate may be leached with dilute sulfuric acid, which dissolves the compounds of copper, forming a solution of cupric sulfate. Dilute ammonium hydroxide may also be used. This causes the copper to pass into solution as the complex ion $\text{Cu}(\text{NH}_3)_4^{+2}$. The solutions obtained by leaching are then electrolyzed to precipitate the copper.

The sulfide ores, which are most impor-

tant, must be smelted. Since these ores contain only a few per cent of copper-bearing compounds, they are first concentrated by grinding, washing with running water, and flotation. The ore is then roasted to remove a portion of the sulfur. In smelting chalcopyrite, which contains a considerable amount of iron, sand is added to convert the iron into ferrous silicate, an easily fusible slag. If the ore contains an excess of silica and alumina (Al_2O_3), limestone is added as a flux. The product of the reverberatory smelting furnace consists of a melted mixture of different metallic sulfides, particularly the sulfides of copper and iron. This mixture is called *malle*. It is mixed with coke and placed in a *converter*, which is made of steel and lined with magnesite brick. A blast of air is admitted near the bottom of the converter to convert iron sulfide into the oxide which, in turn, reacts with silica to form ferrous silicate. This slag is poured off by tilting the converter. A portion of the cupric sulfide is changed at the same time, or by a continuation of the air blast, to cuprous oxide, which then reacts with the remainder of the cupric or cuprous sulfide to form free copper and SO_2 .



The copper is poured into molds and allowed to cool. At this stage of the process, the copper is called "blister" copper, because of the large blisters, or bubbles, formed by escaping gases as the metal solidifies.

Refining consists of remelting the "blister" copper in a silica-lined reverberatory furnace, where the impurities are oxidized and changed into slag. Some copper may be oxidized to cuprous oxide, which is soluble in melted copper. To prevent this occurrence, powdered coal is added to act as a reducing agent, or the melted metal is stirred with sticks of green wood. The copper is next cast into large plates, which are used as anodes in electrolytic cells. Pure sheet copper serves as the cathode, and sulfuric acid is the solution of the cell. The impure

copper passes into solution at the anode, and pure copper deposits on the cathode. The gold and silver in the copper anodes do not dissolve, because they have very weak solution pressures. Consequently, these metals, together with small quantities of palladium, platinum, and other inactive impurities, fall to the bottom of the electrolytic cell, forming "anode mud." The bath contains sodium chloride, which precipitates any silver that passes into solution as silver chloride. This precipitate also becomes a part of the mud. This mud is the source of a considerable portion of the world's silver and gold production, and the recovery of these metals more than pays the cost of refining the copper. The zinc of the impure copper anode dissolves more readily than copper, because of its greater solution pressure, but the zinc ions are less readily discharged at the cathode than the cupric ions. The refined copper deposited on the cathode is about 99.95 per cent pure.

3 Properties and Uses of Copper

Copper is remarkably ductile, malleable, and flexible. The pure metal is an excellent conductor of electricity. Its color is red, when the metal is observed by light reflected from its surface, but it is green, when observed by light that passes through thin sheets. Pure copper cannot be hardened by heat-treatment as steel is hardened. Some of its alloys, however, are very hard and can be tempered by heat-treatment.

The chemical properties of copper are those of a relatively inactive metal. It unites with oxygen, when it is heated in the air, forming CuO and some Cu_2O . It dissolves in solutions of oxidizing acids, such as sulfuric and nitric acids, but in the non-oxidizing acids (HCl) it dissolves slowly and only when oxygen is present. In moist air it is coated with a green deposit of the basic carbonate or sulfate. It combines with sulfur and the elements of the halogen family more readily than with oxygen. Its valences (both positive) are 1 and 2. In the

monovalent state its ions are colorless, while divalent copper is blue. Its compounds are poisonous.

Next to iron, copper is probably the most important of the metals. Its most important use on the basis of the quantity consumed, is in the production of alloys, of which there are several hundred. *Brass* and *bronze* are terms applied to many copper alloys which may vary widely, not only in the percentages of the constituents, but also in the number of metals in the alloys; there are almost 300 different kinds of brass. There are simple brasses that contain only copper and zinc, some brasses contain lead; others contain tin, aluminum, iron, manganese, and nickel. Ordinary bronze is an alloy of tin and copper, but bronzes containing phosphorus, lead, aluminum, iron, silicon, manganese, nickel, zinc, and other elements are also well known. Gun metal contains copper, tin, zinc, and lead; German silver is an alloy of copper, zinc, and nickel, and Britannia metal contains copper, tin, lead, and antimony. The gold in coins and jewelry contains copper and silver. Sterling silver contains 7.5 per cent of copper. Silver and gold coins contain 10 per cent of copper, and nickel coins contain 75 per cent of copper.

Large amounts of copper are used as an electrical conductor for telephone and telegraph lines and in various electrical instruments and devices. Copper is the best conductor of the cheaper metals. The copper used for this purpose must be very pure, since impurities lower the conductivity enormously. A few hundredths of a per cent of arsenic lowers the conductivity as much as 10 or 15 per cent.

Copper is also used in electrotyping. After type has been set up, an impression of it is made in wax and this is covered with graphite, which serves as an electrical conductor. The wax-form is then placed as the cathode in an electrolytic cell containing cupric ions, and the copper is deposited on the letters of the wax plate. The thin metal coating is then removed from the wax and reinforced on

the reverse side with lead which is poured, while molten, upon the copper sheet. Copper also finds use as sheathing for ships, in rollers for printing cotton cloth, in making screens, roofing, trimming for houses, and various utensils used in the kitchen and in industry.

4 Oxides and Hydroxides of Copper

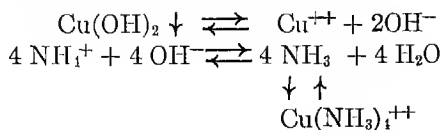
Copper forms two oxides, *cuprous oxide*, Cu_2O , and *cupric oxide*, CuO . Cuprous oxide is found in nature in the form of the mineral called "ruby copper." It may be produced in the laboratory as a reddish-brown substance by gently heating copper in the air, by reducing cupric compounds in the presence of an alkali (NaOH), or by treating cuprous chloride with sodium hydroxide. The last of these methods should produce cuprous hydroxide, but this substance is extremely unstable even at ordinary temperatures, and although it probably forms momentarily, it is changed immediately into cuprous oxide and water. The second method is illustrated by the action of glucose, as a reducing agent, upon Fehling's solution (page 598). This solution is an alkaline mixture containing a cupric salt, sodium hydroxide, and sodium potassium tartrate. In the absence of the tartrate ion, cupric hydroxide precipitates, but when the tartrate is present, a dark blue complex tartrate ion of copper is produced. This ion is very slightly ionized, hence the cupric hydroxide dissolves. If glucose is added, it reduces the trace of the cupric hydroxide which is present to Cu_2O and thus reverses the reaction which previously had formed the complex ion.

Cupric oxide is black. It can be prepared by heating copper powder, wire, or foil in the air or in oxygen. This is the method used to prepare it in commercial quantities. It is also produced when the nitrate or carbonate of copper is heated. If the hydroxide that is precipitated, when sodium hydroxide is added to a solution of a cupric salt, is heated it decomposes into cupric oxide and water.

Cupric oxide is not soluble in water. It dissolves in acids to form cupric salts.

Because of the ease with which copper can be reduced to a valence of one or to the metal, cupric oxide is a good oxidizing agent. As such, it is often used in the analysis of organic compounds to determine the percentage of carbon that they contain. When the carbon is oxidized by the cupric oxide, carbon dioxide is produced, this product is then absorbed in a solution of sodium or potassium hydroxide, and the gain in the weight of the solution is taken as a measure of the quantity of carbon dioxide produced and absorbed. When a coil of copper wire or a copper gauze is heated in the oxidizing flame and then is dipped into a solution containing methyl alcohol, the cupric oxide formed by the oxidation of the copper oxidizes the alcohol to formaldehyde (page 585). This is one of the commonly used methods of detecting methyl alcohol. In addition to its use as an oxidizing agent, cupric oxide is used to remove the sulfur in petroleum products, to color glass and porcelain, and in the manufacture of cupric salts.

As already stated, cuprous hydroxide is a hypothetical substance. When it is formed by the double decomposition of a cuprous salt and a soluble hydroxide, it decomposes at once and completely into the oxide. Cupric hydroxide decomposes when slightly heated. The solubility of this hydroxide in the presence of the tartrate ion has been mentioned (page 674). It is also soluble in ammonium hydroxide, since the cupric ion combines with molecules of ammonia to form a very weakly ionized complex ion

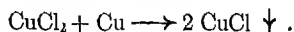


The concentrated solution contains the copper in the form of the compound $\text{Cu(NH}_3)_4(\text{OH})_2$. This solution has a dark blue color, which is distinctive enough to make the reaction a means of detecting copper. The solution is also used in one of the processes (page 616) of manufacturing artificial silk

from cellulose. *Bordeaux mixture* contains cupric hydroxide and calcium sulfate. It is made by adding slaked lime to a solution of cupric sulfate, and is used in the form of a spray as a fungicide and insecticide.

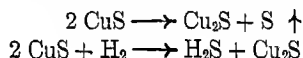
5. Cuprous Salts

Cuprous chloride is a white, slightly soluble salt. It can be prepared by reducing cupric chloride with metallic copper in the presence of hydrochloric acid. Air is excluded as completely as possible to prevent oxidation.



Cuprous chloride dissolves in an excess of HCl to form the compound $\text{H}^+\text{CuCl}_2^-$. This solution is used in the analysis of certain gases that contain oxygen and carbon monoxide. When oxygen is absorbed, the oxychloride, Cu_2OCl_2 , is produced, and in the case of carbon monoxide, the compound $\text{Cu}_2\text{OClH}_2\text{O}$ is formed.

Cuprous sulfide, Cu_2S , may be prepared by heating cupric sulfide in the absence of air and by reducing cupric sulfide by means of hydrogen.



6. Cupric Salts

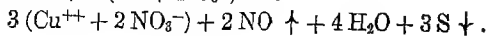
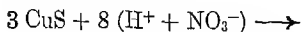
Cupric ion is blue. Its salts are, in general, more soluble and more stable than the cuprous compounds. In aqueous solution, they hydrolyze to some extent, producing acid solutions. This behavior indicates the weakly basic properties of cupric hydroxide. Both normal and basic cupric salts can be prepared. Most of the salts are prepared from the oxide, carbonate, or the free metal. They are usually blue, yellow, or green.

Cupric sulfate is the most important commercial salt of copper. It is prepared by treating the oxide or carbonate with sulfuric acid, by the oxidation of cupric sulfide, or by treating granulated copper with sulfuric acid. Commercially it is prepared in the refining of silver (page 678) or by the oxidation of sulfide minerals, such as chalcopyrite, that contain copper. The pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, crystallizes as blue triclinic crystals from aqueous solutions. This com-

pound is called "blue vitriol" or "blue stone" Other hydrates are known. The anhydrous salt, which is prepared by heating any of the hydrates, is white. Because of its strong tendency to form hydrates, the anhydrous sulfate is used to dry organic liquids. Because it combines with water, giving a blue solution of the hydrate, the anhydrous salt is also used to detect water in liquids, such as alcohol.

Cupric sulfate has a number of uses. It is used in the preparation or manufacture of other copper compounds, Bordeaux mixture (page 675), Fehling's solution, insecticides, germicides, fungicides, paint pigments, and artificial silk. It is used in making the electrolytic bath in the refining of copper, in electroplating, in electrotyping, and in certain electro-chemical cells (page 635). At one time, it was used to produce a green color in canned peas and green beans, but this use has been discontinued because of the poisonous action of copper compounds. It is sometimes used in very small amounts to destroy the algae that grow in municipal water supplies (page 176) and which give the water a disagreeable odor and taste. A minute trace of cupric sulfate is all that is necessary for this purpose.

Cupric sulfide is a black compound. It is one of the least soluble sulfides, and therefore can be precipitated by the treatment of a solution containing a cupric salt with hydrogen sulfide, even in the presence of a moderate concentration of hydrochloric acid (page 497). It can be prepared, also, by the action of sulfur vapor upon hot copper. This salt of copper is important only in analytical procedures by which copper is separated from other metals. Its insolubility in hydrochloric acid provides a means of separating copper from the metals which form sulfides that are soluble in this acid (zinc, cobalt, iron, nickel, etc.). Its very slight solubility in a solution of ammonium sulfide (page 523) makes possible the separation from arsenic, antimony, and tin. Cupric sulfide does dissolve readily in hot dilute nitric acid.



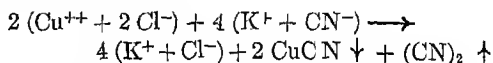
This reaction is used to separate copper from mercury, since mercuric sulfide is not readily soluble in nitric acid.

Other common cupric salts are:

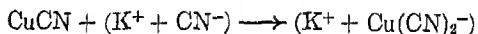
Cupric chloride,	$\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ (green)
Cupric nitrate,	$\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (blue)
Cupric acetate,	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ (green)
Cupric bromide,	CuBr_2 (dark brown)
Basic cupric carbonate,	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (green) <i>malachite</i>
Basic cupric carbonate,	$(\text{CuCO}_3)_2 \cdot \text{Cu}(\text{OH})_2$ (light blue) <i>azurite</i>

7. Complex Cyanogen Compounds

When a solution of sodium or potassium cyanide is added to a solution of a cupric salt, free cyanogen escapes and a precipitate of cuprous cyanide is formed.



If an excess of the alkali cyanide is added, the precipitate dissolves, because of the formation of a complex ion containing univalent copper and cyanogen. This ion is the *cuprocyanide* ion and the potassium compound is *potassium cuprocyanide*. Although other complex cyanides may be produced, this compound is typical.



The cuprocyanide ion is very slightly ionized as shown by the fact that there are not enough cupric ions (Cu^{++}) or cuprous ions (Cu^+) present in its solution to form a precipitate of the sulfide, when hydrogen sulfide is added, or to give a blue color ($\text{Cu}(\text{NH}_3)_4^{++}$) when ammonium hydroxide is added. Potassium cuprocyanide is analogous to potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) and similar compounds.

8 Tests for Copper

The formation of a dark blue solution, containing the complex cupric ammonia ion $\text{Cu}(\text{NH}_3)_4^{++}$, when a solution of a cupric salt is treated with ammonium hydroxide, is often used as a qualitative test for copper. Another test uses potassium ferrocyanide, which gives a rose-colored precipitate of cupric ferrocyanide, $\text{Cu}_2\text{Fe}(\text{CN})_6$. A borax bead (page 541) containing copper has a clear blue color if the bead is made in the oxidizing flame, and an opaque red if made in the reducing flame. The red color, in the

second case, is produced by the reduction of the copper to the free metal

The procedures used in separating copper from other metals have already been described (page 676). Quantitative determinations of copper are usually made by electrolytic methods. The sample is first dissolved in nitric acid, and the copper is then deposited electrolytically upon platinum cathodes, which are weighed before and after the deposition of the metal.

SILVER

9. History and Occurrence

Since silver occurs as the native metal, it has been known since very early times. Because of its bright luster and its slowness to tarnish, it was highly prized by the ancients and was considered by them, as it is today, a precious metal. Until about 1500 B.C. it was more expensive than gold. The Latin name *argentum* means "white." The alchemists associated the metal with the moon, and even now the name "lunar caustic" for silver nitrate is a remnant of this association.

Native silver is seldom pure, it is alloyed with gold, copper, or mercury. It occurs sometimes as large masses or nuggets, but more often it is found as flakes embedded in a rocky matrix. Small deposits of *cerargyrite* or horn silver, AgCl , occur, but the principal compounds in which silver is found are sulfides. The most important of these is *argentite* or *silver glance*, Ag_2S , but others, which contain arsenic or antimony, as well as silver, are also of considerable value. A large amount of the silver which is produced comes from the refining of copper, lead, and nickel, since silver sulfide is often associated, in small amounts, with the sulfides of these metals. Mexico is the largest producer of silver, producing about twice as much as the United States, which ranks second. South America and Canada also produce considerable quantities. Together the two Amer-

icas produce more than 85 per cent of the world's supply, which amounts to a little less than 18,000,000 pounds annually. In the United States the principal silver-producing regions are located in Utah, Idaho, Arizona, and Montana.

10 Metallurgy

Several methods are used to recover silver from its ores. The general principles involved in the processes are described below.

(1) *Parke's Process* This process is widely used to recover the silver that occurs in lead and copper ores, and therefore serves also as a means of purifying the lead and copper. When silver ores are treated by this process, they are mixed with lead ores before they are smelted. The product of the smelter is an alloy of lead and silver. The Parke's process deals directly with this alloy or with impure lead obtained in the smelting of lead ores. The alloy is melted in large kettles, and about one per cent of its weight of zinc is added and stirred with it. The zinc is added as a solvent for the silver, which is much more soluble in zinc than it is in lead. Zinc also dissolves gold and copper readily. Since zinc is lighter than lead, and since the two metals do not mix, the zinc rises to the top and bungs with it most of the silver, gold, and copper which were originally present in the lead. As the mass cools, this layer forms a crust upon the surface of the molten lead. It is removed by large skimmers, and is heated in a retort. The zinc distills off and is used again. The residue remaining in the retort contains silver, gold, and copper. The silver is purified by electrolysis or by the process of cupellation (see below).

(2) In the process used for *anode mud* (page 673) the more active metals are dissolved in dilute sulfuric acid. The residue of insoluble metals is first dried and later is heated with a mixture of some oxidizing agent, such as sodium or potassium nitrate, sodium carbonate, and sand. This treatment converts the base metals, first into oxides and then into slag (silicates), which can be removed readily from the silver and other precious metals.

(3) *Leaching Processes* Ores containing silver sulfide are sometimes roasted to produce silver sulfate, and the product is leached with water,

in which silver sulfate is soluble. The silver is precipitated and recovered from this solution by adding copper. Cupric sulfate is a valuable by-product of this process (page 675).

One of the most important methods of recovering silver from its ores depends upon the solubility of the metal and many of its compounds in solutions of the alkali cyanides (NaCN or KCN). Complex cyanides, such as $\text{NaAg}(\text{CN})_2$, are produced. This method of getting silver into solution is applicable to ores containing silver chloride or small scattered particles of metallic silver, if the ores are finely pulverized in a stamp mill before they are treated with a solution of the cyanide. Silver sulfide and large grains of the chloride and of the free metal dissolve very slowly. To hasten solution sulfide ores are sometimes roasted with sodium chloride to form silver chloride, which is then dissolved in the cyanide solution. Silver is recovered from the cyanide solutions by adding powdered zinc or aluminum to displace the silver.

(4) *Amalgamation* Ores containing metallic silver or silver chloride may be treated with mercury to form an amalgam, which is separated from the earthy material of the ore and distilled in a retort. Silver remains in the retort, while the mercury is distilled, condensed, and used again. The metallic silver of the ore alloys (amalgamates) with the mercury directly, while the silver chloride is first converted by the mercury into metallic silver and mercurous chloride.

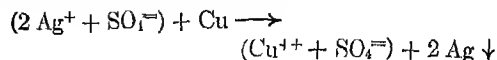
11. Refining

Whatever process is used to recover silver from its ores, the metal must be refined. Only two methods of refining will be discussed here.

(1) *Electrolytic Process* This process is similar to the electrolytic refining of copper. Pure silver is used as the cathode and impure silver as the anode, with a solution of silver nitrate and nitric acid serving as the electrolyte. Silver dissolves at the anode and is deposited as loose crystals on the cathode.

(2) *Cupellation* An alloy of silver with lead is heated in a shallow hearth furnace. The hearth is made of porous material, such as cement. A current of air blows over the hearth. This causes lead and other impurities to be oxidized, and the oxides are removed by vaporization, by

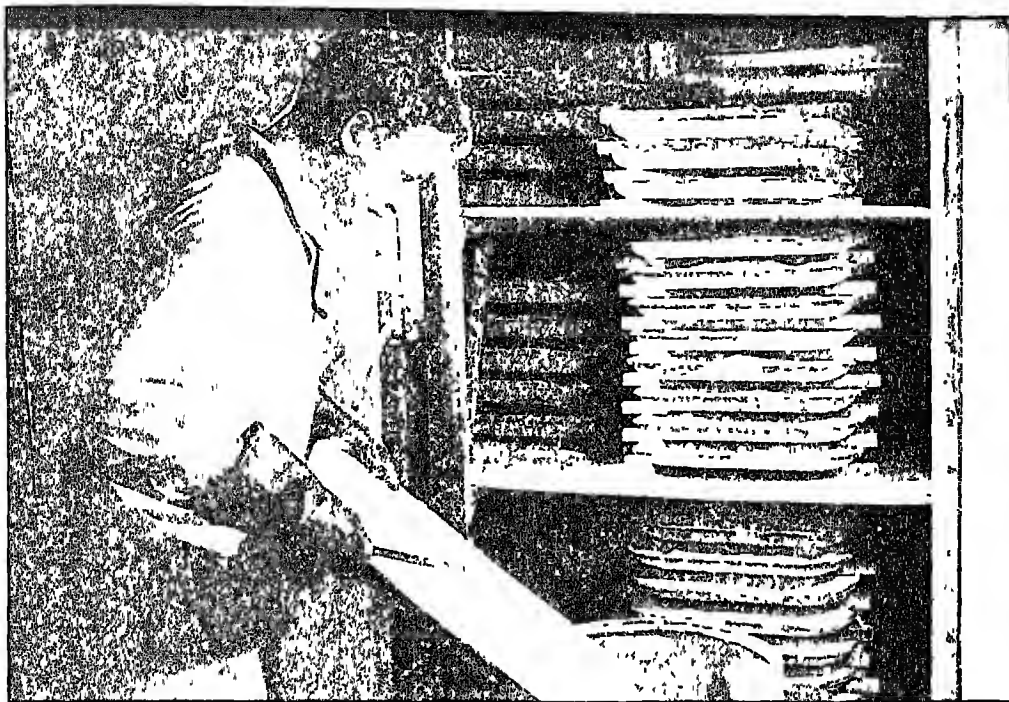
sweeping, or by absorption in the lining of the furnace. The silver, still containing gold, copper, and small amounts of other metals, is cast into ingots of *doré bullion*. Gold is separated from silver by electrolysis, or by treating the bullion with hot concentrated sulfuric acid, which changes the metals, with the exception of gold, into sulfates, most of which are soluble. The gold is recovered from the insoluble residue or "mud," and the silver is displaced from the solution by copper.



12. Properties of Silver

Silver is a heavy, white metal. It is intermediate between gold and copper in hardness. It is an excellent conductor of electricity and heat and is one of the most malleable and ductile of the metals. It alloys readily with almost all of the heavy metals, and although some pure silver may be used as a jewelry-metal, alloys of silver are most often used for this purpose as well as for coins, tableware, and similar articles. These alloys are harder and therefore more durable than pure silver.

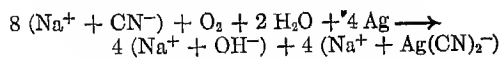
Chemically, silver is classed as one of the least active metals. It lies below hydrogen and well toward the bottom of the electrochemical series. It is attacked more readily by sulfur than by any other element. Sulfur itself, and many sulfur-compounds, produce a black coating of silver sulfide upon the surface of any article made of silver. This accounts for the tarnishing of silver when it is exposed to air containing even traces of such compounds. "Oxidized" silver is actually "sulfidized"; it is silver which has been treated with a solution of sodium sulfide, or with another soluble sulfide, producing a film of black silver sulfide. *Stainless silver* is a non-tarnishing alloy of silver, copper, and antimony. Silver is attacked by the halogens, but the action is slow and usually affects only the surface, because the silver halide that is formed protects the metal from further action. Silver does not combine directly with oxygen, even at ele-



Courtesy of du Pont Company

Figure 306 Silver Salt to be Used in Making Airplane Motors
Silverplated bearings withstand the high loads and speeds demanded of modern planes.

vated temperatures, and it does not combine with carbon, hydrogen, or nitrogen. It dissolves in the oxidizing acids (HNO_3 and H_2SO_4) to form salts (AgNO_3 and Ag_2SO_4). The solubility of the metal in solutions of the alkali cyanides has already been mentioned (page 489)



It does not dissolve in dilute acids or in solutions of alkalis. Metallic silver has a number of uses. Because of its slowness to tarnish and pleasing appearance, it is used to electroplate cheaper metals in the manufacture of tableware and many ornaments. Almost all mirrors are made by depositing silver upon glass. Its use to make coins, jewelry, silver nitrate, and the silver halides has been mentioned previously.

13. Mirrors

When a solution of silver nitrate containing a

limited quantity of ammonium hydroxide is treated with formaldehyde, glucose, or certain other organic compounds, the silver is reduced to the free metal, which is deposited on the walls of the containing vessel. The ordinary silver mirror is made in this manner by causing the silver to deposit on the glass. Some mirrors are made by using thin coats of aluminum foil, which is an excellent reflector. A coating of lead sulfide is also used; this substance forms a mirror that reflects without glare. At one time, mirrors were made by coating glass with tin amalgam, an alloy of tin and mercury.

14. Silver Oxide, Ag_2O

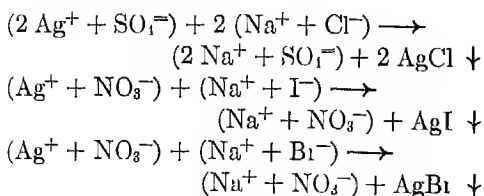
Silver hydroxide is a hypothetical substance. Whenever a soluble hydroxide is added to a solution containing a silver salt, the hydroxide of silver, which we might expect to form, decomposes spontaneously to form the oxide, Ag_2O . Despite this behavior, silver hydroxide must exist to a slight extent in such mixtures; pure silver oxide reacts

sufficiently with water to produce a solution that changes the color of red litmus to a pronounced blue, an indication that silver hydroxide is presented in the solution. The fact that the soluble silver salts of the strong acids are not hydrolyzed appreciably shows that silver hydroxide, to the extent that it exists in solution, is a highly ionized, strong base. This is one of the few points of similarity between silver and the alkali metals of group one.

Like the oxides of many of the heavy metals, silver oxide is not very stable. When it is heated, even at 200°–250°, the decomposition is rapid. Silver oxide in combination with certain substances of a protein nature is used as a common antiseptic. The silver compounds in these mixtures are colloiddally dispersed. Of these antiseptics "argyrol" is probably the best known. Silver peroxide is a black compound, produced by the action of ozone upon silver.

15. Compounds of Silver and the Halogens

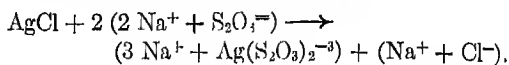
Of the four halides of silver, only silver fluoride, AgF , is readily soluble. The chloride, bromide, and iodide dissolve very slightly, and the solubility decreases with the increasing atomic weight of the halogen, thus, silver iodide is the least soluble of the four salts. The fluoride is prepared by treating the oxide of silver with hydrofluoric acid. The other silver halides can be prepared in a similar manner and also by simple precipitation reactions, in which the halogen acid or a soluble chloride, bromide, or iodide (NaCl , NaBr , and NaI) is added to a solution of a silver salt.



These three silver halides form curdy precipitates. Freshly prepared silver chloride is white, silver bromide is pale yellow; and

silver iodide has a brighter yellow color. All three salts are sensitive to light and are used in photography (page 681).

Silver chloride and silver iodide combine with pure gaseous ammonia to form compounds analogous to hydrides: $2 \text{AgCl} + 3 \text{NH}_3$, $\text{AgCl} + 3 \text{NH}_3$, and $2 \text{AgI} + \text{NH}_3$. Silver chloride dissolves in an excess of ammonium hydroxide, forming the complex ion $\text{Ag}(\text{NH}_3)_2^+$. It also dissolves slightly in concentrated hydrochloric acid, forming the complex acid, $\text{H}_2^+\text{AgCl}_3^-$. In a solution of potassium or sodium cyanide it forms the complex cyanide, $\text{KAg}(\text{CN})_2$ or $\text{NaAg}(\text{CN})_2$ (page 679). In a solution of sodium thiosulfate it is converted into the complex ion, $\text{Ag}(\text{S}_2\text{O}_3)_2^{2-}$.

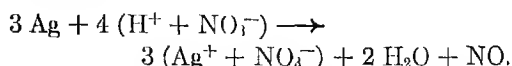


The solubility of the silver halides in a solution of sodium thiosulfate is the basis of the fixing process for plates, films, and prints in photography (page 682).

The tendency of silver salts to dissolve in sodium thiosulfate, hydrochloric acid, ammonium hydroxide, or potassium cyanide is explained by the very slight ionization of the complex ions produced in the different solutions. Though the formation of these complexes the concentration of the silver ion is lowered until the solubility product of the silver halide is not exceeded. As long as this condition exists the silver halide, of course, continues to dissolve. Whether or not all of it dissolves depends upon the quantity of cyanide, thiosulfate, chloride, or ammonia which is added.

16. Silver Nitrate

Silver nitrate, sometimes called "lunar caustic," is the most widely used silver compound. It is prepared by dissolving silver in nitric acid.



The solid salt is used, in the form of sticks, to cauterize wounds. Its use for this purpose depends upon the strong oxidizing action of silver nitrate and upon the precipitation of protein compounds by silver ion. The pure salt is not affected by light but

when placed upon the skin, black metallic silver is deposited by the action of reducing agents. Similar deposits of silver are produced when a solution of the salt is placed upon cloth. For this reason a solution of silver nitrate is used either alone or as an ingredient in marking inks.

17 Tests for Silver

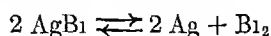
The separation of silver from the other metals is easily accomplished, since silver chloride is one of three slightly soluble chlorides (AgCl , HgCl , and PbCl_2). If hydrochloric acid or a soluble chloride is added to a solution containing the ions of the common metals, only these three chlorides, and possibly antimony and bismuth oxychlorides, precipitate. The oxychlorides of antimony and bismuth may be prevented from precipitating by the addition of hydrochloric acid (page 525). From the residue consisting of the chlorides of silver, mercury (-ous), and lead, the lead chloride is first removed by washing the residue with hot water, the silver chloride is then separated from mercurous chloride by treating the residue with a solution of ammonium hydroxide, in which the silver salt is soluble. After filtration, the filtrate is acidified with nitric acid and silver chloride reprecipitates. Other methods are sometimes used to detect silver. These depend upon the colors of the precipitates that silver forms with different anions. Thus, silver phosphate, Ag_3PO_4 , is yellow, silver chromate, Ag_2CrO_4 , is brick-red, and silver iodide, AgI , is yellow.

18. Photography

The most familiar photochemical reaction is that which is employed in photography, this reaction involves the decomposition of the silver halides when they are exposed to the light. This effect of light was discovered by Scheele in the latter part of the eighteenth century. He found that silver chloride becomes dark and loses weight in the sunlight. He also found that the loss in weight is due to the loss of chlorine. The darkening is

due, therefore, to the liberation of metallic silver. In 1839, Daguerre discovered a method of producing pictures by means of a similar reaction. He exposed, in a camera, a plate which had been coated with silver iodide, thus producing an invisible or latent image of the object before the camera at the time of the exposure. He developed the image by exposing the plate to mercury vapor. This was the method of producing the first of the so-called *daguerreotypes*.

Modern photography also depends essentially upon the effect which light produces when it falls upon a silver halide, very often silver bromide. The reaction



is reversible. Sunlight aids the reaction toward the right, but in the darkness and in the presence of the free halogen the reaction is reversed. The photographic plate or film consists of a glass plate, or a film made of cellulose nitrate or acetate. One side is covered with a light-sensitive coating of gelatin in which there is a colloidal suspension of the silver halide. The *speed* of the plate depends upon the size of the particles of the silver salts, the smaller the particles, the more slowly light affects them. The size, ordinarily, is of the order of 2 to 3 μ (1 μ = 0.001 mm). In the camera a lens focuses, upon the plate, the light which is reflected from the object to be photographed. When the shutter of the camera is opened, this light strikes various portions of the gelatin film with different intensities. The light from dark objects, which reflect feebly, is less intense than that reflected from white or brighter parts of the subject before the camera. Since the effect of the light upon the silver halide varies with the intensity of the light, an invisible image is produced upon the plate or film.

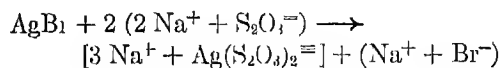
The decomposition of the silver halide is not completed by the brief exposure, but the portions affected by the light are more easily reduced when the entire plate is treated with a reducing agent. This treat-



Figure 307 Bars of Silver to be Used in the Production of Photographic Film and Paper

ment is called *developing* and the reducing agent is the developer. For this purpose a solution of pyrogallol, hydroquinone, or some other good reducing agent of a similar character is used in the presence of sodium carbonate. The developer may also contain a preservative, such as sodium sulfite and a retarder, usually potassium bromide. In this developing solution the silver halide is reduced to metallic silver, those portions of the plate which have been effected by the most intense light being more completely reduced and consequently showing darker deposits of metallic silver. The portions of the plate which have not been exposed to light are not affected by the developer unless the plate is kept in the solution for a longer period of time than is necessary to bring out the picture. This treatment is carried out in the dark. Before it can be exposed to the

light, the developed plate or film must be treated in a fixing bath, which is a solution of sodium thiosulfate (page 387). This solution dissolves all of the silver halide which has not been reduced.



The plate is then washed and dried. It is now the *negative*. In it the directions are reversed to those in the subject, the dark portions of the subject are represented by the light portions of the negative, where no silver has been deposited. The negative is used to make the *prints* or positives. A sheet of paper which is covered with a gelatin suspension of silver halide (bromide or chloride, usually) is placed behind the negative, which is exposed to light, usually an artificial

light. The effect is the same as in the making of the negative. The portions of the plate or film which are free of silver permit the full intensity of the light to act upon the silver halide of the paper. Those portions upon which silver is deposited permit less light to act upon the paper, the intensity depending upon the thickness of the silver deposit. After exposure, the print is developed and fixed in the same manner as the negative. Most printing papers are coated with a suspension of silver bromide or a mixture of the bromide and chloride. If the silver chloride alone is used, no developer is needed, since the image, instead of being latent, is immediately visible without the use of a developer. Such papers are used in making *proofs*. After exposure, the excess of unaffected silver chloride is removed by the fixing bath and the paper is washed in a solution of a gold or platinum salt. Since it is higher in the electrochemical series, the silver replaces either gold or platinum from the solutions of their salts, and these metals are deposited on the paper in its place. If gold is used, the proof is reddish brown in color, and if a platinum bath is used, it has a lustrous, gray, metallic color.

The sensitivity of a silver halide to light may be remarkably increased by the use of sensitizers, which are usually dyes. These are effective because they absorb wave lengths of radiations which have little effect upon the silver halides, when the halides are used without sensitizers. The halides do not absorb these radiations, which are in general those of the longer wave lengths — red and infrared — and consequently are not affected by them. If the sensitizer absorbs these rays, it appears that the energy thus acquired is at least partially effective in starting the decomposition of the silver salt. The sensitivity also depends upon the gelatin and upon the impurities which it may contain. By the use of sensitizers better pictures can be made in mist and fog, which are more readily penetrated by infrared radiation than by ordinary light.

GOLD

Gold was at least one of the first metals, and probably the first, used by man. Its occurrence in the native state permitted primitive peoples to obtain it in moderate quantities before there was any knowledge of metallurgical processes. Its rarity, pleasing appearance, softness, and durability made gold highly desirable for jewelry, ornaments, and even for the decoration of buildings. Throughout human history, gold has played an important part as a standard of value and a medium of trade.

19 Occurrence

Gold is found in nature almost always in the free state. It sometimes occurs as nuggets, but it is more frequently found as small flakes scattered in veins of quartz or in alluvial sands. Nuggets weighing as much as 160 pounds have been found. Native gold usually contains some silver, platinum, and related metals. It is present in small quantities in the sulfide-ores of metals, such as copper and lead. The tellurides of gold and silver occur as mixed crystals in the mineral called *sylvanite*, a telluride of silver and gold. The chief gold-producing regions of the world are Africa, which supplies more than half of the world's production, the United States (about 10 per cent), Canada (10 per cent), Europe and Asia (about 6 per cent each), Mexico, Australia, and Central America. Sea water contains traces of gold. The world's production, before 1939, was about 35,000,000 Troy ounces per year.

20 Mining and Metallurgy

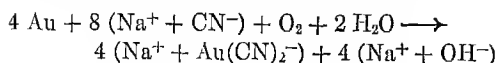
In the "gold-rush" days of California, gold was obtained by *panning*. This method was used to recover the gold found in alluvial sands. The material was placed in shallow pans and washed with water, the sand was washed away over the edge, and the flakes of gold collected on the bottom of the pan. Placer mining made use of the same principle on a larger scale. The deposits were

placed in long troughs, and the sand was carried away by a stream of water. The gold particles settled to the bottom of the troughs and were caught and held there by small cleats. These methods later gave way to "hydraulic" mining, in which powerful streams of water are directed against the sand, which is washed into sluices in which the gold is collected by settling, and the lighter material is washed away.

The gold that occurs in quartz veins is recovered by one of three processes. These processes may be used, also, on alluvial deposits. First of all, the quartz ore must be pulverized in a stamp mill.

(1) *Amalgamation.* The use of mercury in the recovery of gold has been practiced for almost 2500 years. Gold dissolves in mercury, forming an amalgam, which is easily separated from quartz, soil, and other worthless materials. The pulverized ores are made to flow in streams of water over copper plates, whose surfaces are amalgamated. The gold dissolves in the mercury and the amalgam is scraped off the plates. In sluice or *placer* mining mercury is sometimes placed between the cleats in the bottom of the trough to form the amalgam. To separate the gold from the mercury, the mixture is placed in a retort, and the mercury is distilled.

(2) *The Cyanide Process.* The process has made possible the recovery of gold from low-grade ores, from material that has already been worked over by panning or by sluice or placer mining, and from the discarded materials of the amalgamation process. The gold ore is treated with a dilute solution of sodium or potassium cyanide in the presence of air. Gold is converted into a soluble complex cyanide by the following reaction:



This reaction is slow, and each batch of ore must remain in contact with the cyanide solution for several days. In working rich ores, the larger particles of gold are first removed by the amalgamation process, and the remainder is recovered by means of a cyanide solution. This gold is finally recovered from this solution by adding zinc to precipitate it or by means of electrolysis.

(3) *The Chlorine Process.* This process depends

upon the action of chlorine upon gold. The chlorine is purchased in steel cylinders or is produced on the spot by allowing sulfuric acid to react with bleaching powder. Auric chloride, AuCl_3 , is produced by the direct combination of the elements. Gold is recovered by the electrolysis of a solution of this compound.

Refining. The gold produced by any of these methods must be refined. This is usually done by the electrolysis of gold cyanide solutions. The older method used sulfuric acid to dissolve silver and other metals. Crude or impure gold, usually consisting of alloys of gold, silver, and copper, is sometimes refined by first melting it and then treating it with chlorine. The chlorides of silver and copper form first, and as they form they are skimmed off the surface as solids. Water is then added to the gold that remains, and the continued action of chlorine converts the metal into auric chloride, from which gold is recovered by electrolysis. Gold is also refined by cupellation (page 678), in which other metals (but not silver) are oxidized and removed as oxides, which are absorbed by the bone-ash hearths of the cupellation furnace.

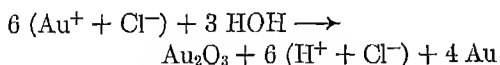
21 Physical Properties of Gold

Gold is the most malleable and ductile of all the metals. Gold foil only 0.00001 mm in thickness can be made by rolling the metal. Pure gold is yellow. The yellow gold used in coinage and in jewelry is alloyed with copper. This alloy has a redder color than pure gold, it is also harder. Gold alloys with a green tint are produced by adding silver or cadmium. White gold contains silver, or, sometimes, palladium or nickel. The purity, or fineness, of gold is expressed in carats, which indicate the number of parts of gold in 24 parts of the metal. Thus, a 14-carat (yellow) gold ring contains $41\frac{2}{3}$ per cent of copper (10/24), and an 18-carat ring contains 25 per cent of copper. The gold used in United States gold-coins is 21.6 carats; this is 90 per cent gold. Gold-plated jewelry and ornaments are made by electroplating gold on copper from a solution of sodium or potassium aurocyanide ($\text{NaAu}(\text{CN})_2$). Alloys containing more than 18-carat gold are too soft for most uses. Gold is easily pre-

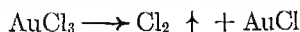
paired in the colloidal state by reducing gold salts in solution or by the Biedig arc method (page 548). When a dilute solution of a gold salt is treated with a solution of stannous chloride and stannic acid, the gold is reduced to the free metal by the stannous chloride. When the mixture is heated, a colloidal state of the stannic acid is produced and adsorbs the fine particles of gold. This gives a deep purple precipitate called *purple of Cassius*.

22. Chemical Properties and Compounds of Gold

Chemically, gold is an inactive metal. It is not attacked by oxygen or by common acids, such as HCl, HNO₃, or H₂SO₄. It combines with chlorine to form auric chloride, AuCl₃, at temperatures above 150°. It also combines slowly with bromine and with iodine. Fluorine scarcely attacks it at ordinary temperatures, but the reaction is somewhat more pronounced at higher temperatures. It dissolves in aqua regia and in chlorine water to form auric chloride. When heated with alkalis, such as KOH, the gold is attacked and is converted into soluble alkali *aurates* (KAuO₂). Gold's common valence is positive 3. It also displays a valence of positive 1, but the *aurous* compounds tend to change spontaneously in solution into *auric* compounds and metallic gold.



When heated, the auric compounds decompose to give either metallic gold or the corresponding aurous compounds.



Auric hydroxide is amphoteric, acting slightly more like an acid than a base. When heated slightly it gives the oxide, Au₂O₃. It dissolves in acids to form salts, such as auric chloride, AuCl₃. With bases it acts as auric acid, H[AuO₂(H₃AuO₃ - H₂O)], and forms aurates, such as KAuO₂. The sulfides, Au₂S and Au₂S₃, resemble the sulfides of arsenic,

antimony, and tin in that they dissolve in ammonium polysulfide (page 523) to form thio-salts, ammonium thioaurite, NH₄AuS, and ammonium thioaurate, (NH₄)₃AuS₃ or NH₄AuS₂.

Gold forms many complex compounds. Both aurous chloride and auric chloride dissolve in an excess of hydrochloric acid, aurous chloride forms chloroaurous acid, H[AuCl₂], and auric chloride forms chloroauric acid, H₂AuCl₄. The sodium salt of the latter is used in photography to tone prints. The cyanide complexes, KAu(CN)₂ and KAu(CN)₄, have already been mentioned (page 684). They are used in electroplating cheaper metals with gold. Unlike the salts of silver, gold (auric) salts are highly hydrolyzed in solution. This behavior is in keeping with the amphoteric nature of Au₂O₃ and Au(OH)₃.

In addition to the compounds in which gold is univalent or trivalent, the element also forms a number of very unstable compounds in which it is divalent. These correspond to the unstable oxide, AuO.

SUMMARY

The differences between copper, silver, and gold and the metals of the alkali family may be summarized as follows:

(1) Copper, silver, and gold are not readily oxidized. They are found at the bottom of the electrochemical series, while the alkali metals are at the top.

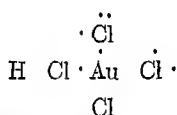
(2) The alkali metals have a valence of positive 1 in all of their compounds. The more stable and familiar forms in which copper and gold appear in their compounds, however, are divalent and trivalent, respectively.

(3) The oxides of the alkali metals are decidedly more basic in nature than those of the metals of the B division.

(4) Copper, silver, and gold display a pronounced tendency to form stable complex ions.

These differences are explained by the two types of atomic structure possessed by the alkali metals on the one hand and by copper, silver, and gold on the other. In each case a single valence

electron lies in the outermost shell, but in the atoms of the alkali metals this electron lies above a very stable group of eight electrons, from which additional electrons can be removed only with great difficulty. For these atoms, therefore, the removal of one electron to form univalent ions is about the only possible condition that can result from chemical reactions. The single valence electron of a copper, silver, or gold atom overlies a group of eighteen electrons, some of which may be removed in ordinary kinds of chemical change, giving the element a valence greater than one. The formation of complex ions by these elements depends upon their ability to share two or four pairs of electrons with other atoms. These electrons belong in the outermost shells of the copper, gold, and silver atoms and constitute a group of four or (usually) eight electrons above the group of eighteen in the shell immediately beneath them. The sharing of electrons by gold is illustrated by the following formula for chloroauric acid:



ZINC

Zinc has been known as a pure metal and as a constituent of brass for a very long time. Articles made of zinc long before the beginning of the Christian era have been discovered. It was certainly one of the first metals to be produced from its ores by simple metallurgical processes. In early times, however, not pure zinc but an alloy of copper and zinc (brass) was produced by smelting ores containing both metals. Zinc was not recognized as a distinct substance until some time in the seventeenth century.

23 Occurrences and Metallurgy

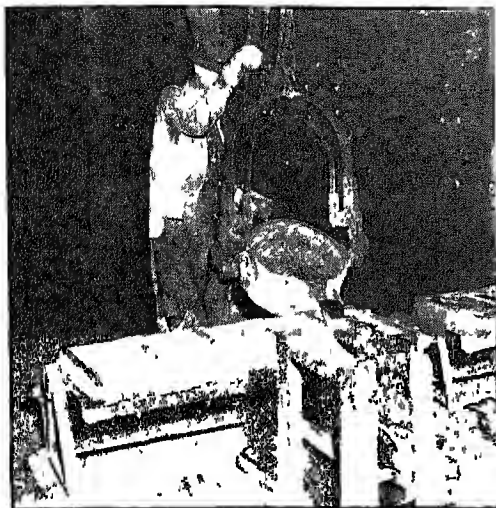
The occurrence of zinc is limited to deposits in scattered localities on the earth's surface. The most important ores are *sphalerite*, ZnS , *smithsonite*, ZnCO_3 , *willemitte*, Zn_2SiO_4 , *franklinite*, ZnFe_2O_4 with iron and manganese replacing some of the zinc; *zincite*, ZnO , and *calamine*, $\text{Zn}_2\text{H}_2\text{SiO}_5$. In the United States the chief zinc-producing



Courtesy of United States Steel Corporation

Figure 308 Zinc Furnace

Zinc ore is reduced in the retorts and the vapor is condensed to liquid zinc in the condensers, the ends of which are seen projecting from the furnace. The gas that burns at the ends of the condensers is carbon monoxide.



Courtesy of Eagle-Picher Sales Company

Figure 309. Pouring Zinc Spelter from Ladle

localities are in Oklahoma, Missouri, Kansas, and New Jersey. The world's production is about 2,000,000 metric tons each year, the United States produces about 700,000 tons.

The older metallurgical treatment of zinc ores consists of roasting the sulfide or igniting the carbonate to form the oxide and then reducing the oxide by means of carbon. The ore is first crushed and then concentrated by flotation (page 556). After roasting or ignition, the concentrated material is heated with coal in earthenware retorts, which are about five feet long. The retorts are placed in a slightly sloping position in gas-fired furnaces. Condensers are placed over the mouths of the retorts. As rapidly as the zinc is produced by reduction, it distills and is condensed in these receivers. Zinc is also produced in a vertical type of retort. The temperature of the retort is about 1200°. If the temperature of the condenser is above 419.4° (the melting point of zinc), the metal is collected in the liquid state and can be drawn off and allowed to solidify in molds. Zinc dust, containing five per cent or more of zinc oxide, first collects in the receivers, when the temperature is low. The zinc that comes from the molds is called *spelter*. It contains, in addition to zinc, small amounts

of iron, cadmium, lead, arsenic, and carbon. Some of these impurities can be separated by redistilling the spelter in a vacuum or in an atmosphere of hydrogen to prevent oxidation.

More modern metallurgical practice involves, first, the leaching of the roasted ore with a solution of sulfuric acid. This gives a solution of zinc sulfate from which the zinc is recovered by electrolysis. The less active metals, such as copper, silver, cadmium, and lead are precipitated by the addition of metallic zinc before the solution is electrolyzed. Very nearly pure zinc can be produced by the electrolytic method.

24. Physical Properties

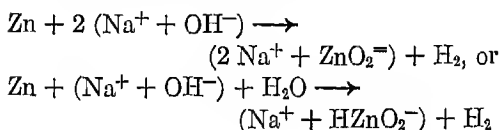
Freshly polished zinc has a white metallic luster, but because of tarnishing its more familiar appearance is blue-gray. At ordinary temperatures, it is hard, crystalline, and brittle. If heated to 100°–150°, it becomes malleable enough to be rolled into thin sheets and can be drawn into wire. Above 200° it loses this property and becomes brittle again. This behavior indicates the existence of allotropic forms of the metal. Granulated or *mossy* zinc is made by pouring melted zinc slowly into water.

25. Chemical Properties

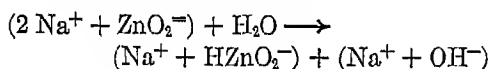
When freshly polished zinc is exposed to moist air, the surface is soon coated with a basic carbonate, $\text{Zn(OH)}_2 \cdot \text{ZnCO}_3$. When heated above 600°, zinc burns in air with a bluish-white flame to form ZnO . It also burns when the dust or small particles of the metal are heated with sulfur. It does not displace hydrogen from cold water, or even from boiling water, but it does displace this element from steam if strongly heated. Impure zinc dissolves readily in dilute acids. When treated with nitric acid, it liberates the lower oxides of nitrogen (NO and N_2O) and may also form ammonia (page 484). From dilute hydrochloric and sulfuric acids it liberates hydrogen. Pure zinc reacts very slowly with these acids because of the

tendency of the hydrogen which is liberated to collect on the surface, forming a protective layer. Ordinary, commercial zinc dissolves readily in dilute acids, because it contains, as impurities, iron, copper, and other metals. Small particles of these metals on the surface of zinc form couples (page 637), and hydrogen is discharged on them rather than on zinc.

Zinc dissolves, also, in solutions of strong bases, liberating hydrogen and forming *zincates*. This behavior indicates that zinc has non-metallic as well as metallic properties. The reaction with NaOH is as follows:



The product of the first of these reactions is sodium zincate, and the acid salt is formed in the second case. Except in the presence of an excess of NaOH, the acid salt is more likely to form because of the tendency of the normal zincate to hydrolyze:



26. Uses of Zinc

We are most familiar with zinc as the protecting covering on *galvanized* iron. The surface of the iron is coated with zinc by electroplating, by dipping the iron sheet into melted zinc, or by covering the surface of the iron with a spray of melted zinc. The electroplating process is growing in importance. *Shearized* iron is produced by covering the iron with a mixture of zinc dust and zinc oxide and heating it in a revolving drum. Although it is a moderately active metal, zinc resists corrosion, because a thin but firmly attached layer of basic zinc carbonate is formed on the surface of zinc exposed to the air, and the coating protects the metal from the further action of oxygen. The protective action of the zinc coating on galvanized iron is explained, in part, by the exclusion of air from the surface of the iron.

When a scratch is made through the zinc, or the layer of zinc becomes broken in any way, the zinc further protects the iron by acting as the more active metal of the couple. The zinc rusts while the iron remains unaffected for a time.

Zinc is also used in manufacturing many alloys: brass, Babbitt metal (page 524), German silver, and others. It is also used in batteries and dry cells (page 636), in separating silver and gold from lead (page 677); and in weather-stripping, gutters, and cornices. It has many uses in the laboratory as a reducing agent.

27. Zinc Oxide, ZnO and Zinc Hydroxide, Zn(OH)₂

Zinc oxide is a white powder at ordinary temperatures. It turns yellow when heated, but becomes white again as it cools. It is made by burning metallic zinc, by heating the basic carbonate, $\text{Zn}(\text{OH})_2 \cdot \text{ZnCO}_3$, or by roasting the sulfides of zinc. It is used as a paint pigment called *zinc white*. Since zinc sulfide is also white, paints containing zinc oxide (instead of white lead) do not

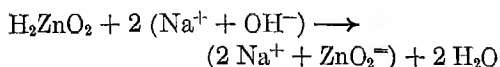


Courtesy of Eagle-Picher Sales Company

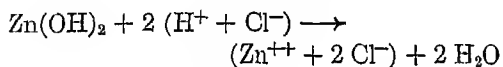
Figure 310 The Open Door of a Zinc Oxide Furnace

darken when they are exposed to an atmosphere containing hydrogen sulfide. One of the important uses of zinc oxide is in the manufacture of automobile tires (page 577) and other rubber goods. It is also used in manufacturing glass and enamels, and in preparing medicinal ointments.

Zinc hydroxide may be precipitated by adding a soluble hydroxide to the solution of a zinc salt. The precipitate dissolves in an excess of sodium hydroxide or potassium hydroxide, forming a solution of sodium or potassium zincate, Na_2ZnO_2 or K_2ZnO_2 .

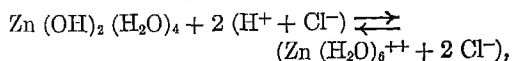


It dissolves in acids to form zinc salts



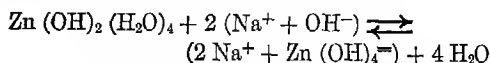
Zinc hydroxide, therefore, is an amphoteric hydroxide.

We have already pointed out (page 548) that the precipitate produced when a soluble hydroxide is added to solutions containing the ions of any one of several of the metals is probably a hydrous oxide instead of a hydroxide. For example, the precipitate that is produced by adding sodium hydroxide to a solution containing Zn^{++} ions should be represented as $\text{ZnO} \cdot n\text{H}_2\text{O}$ rather than as $\text{Zn}(\text{OH})_2$. Since the hydrous oxide is of variable water content, and since the reactions are more easily understood when the precipitate is represented by the formula of the hydroxide, the equations are usually written as we have shown them above. Frequently, however, the compound formed by adding hydroxyl ions to a solution containing Zn^{++} ions is assigned the formula $\text{Zn}(\text{OH})_2(\text{H}_2\text{O})_4$, which is really the formula of hydrated zinc hydroxide. As written, this formula shows zinc as having a co-ordination number of six. When this substance acts as a base with an acid the reaction may be written as



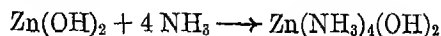
which indicates the presence of the hydrated zinc ion, $\text{Zn}(\text{H}_2\text{O})_6^{++}$ in the resulting solution of zinc

chloride. The reaction, as an acid, with sodium hydroxide may be written as



The salt $\text{Na}_2\text{Zn}(\text{OH})_4$ may be regarded as the equivalent of $\text{Na}_2\text{ZnO}_2 \cdot 2 \text{H}_2\text{O}$.

Zinc hydroxide dissolves readily in ammonium hydroxide because of the formation of a very slightly ionized complex ion, $\text{Zn}(\text{NH}_3)_4^{++}$.



28. Zinc Chloride (ZnCl_2)

Zinc salts are prepared by treating zinc or zinc oxide with the appropriate acid. To produce zinc chloride, for example, an excess of hydrochloric acid is used. The resulting solution is evaporated to dryness, and the residue is fused to remove the last traces of water. The excess of acid is used to prevent hydrolysis during evaporation. In the absence of the acid, zinc chloride hydrolyzes to produce the basic chloride, ZnOHCl , or the oxychloride, Zn_2OCl_2 . Zinc chloride is used to preserve wood and to manufacture parchment paper. These uses depend upon the fact that an aqueous solution of zinc chloride acts upon cellulose to partially dissolve it and to form a gelatine-like mass. Its aqueous solution is also used to clean the surface of metals before soldering. This use depends upon the hydrolysis of zinc chloride to form hydrochloric acid, which dissolves the oxides coating the metals to be soldered.

29. Zinc Sulfate (ZnSO_4)

This salt is prepared by roasting ores containing zinc sulfide. Some zinc sulfate is produced by oxidation. This is dissolved by leaching the material with water and is recovered by crystallization. The heptahydrate, $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$, which crystallizes from solutions, is called *white vitriol*. It is used in medicine, as a mordant in dyeing, and in the manufacture of lithopone (page 669).

30. Tests for Zinc ion

The separation of zinc from the other common metals depends upon the following behavior of its compounds:

(1) The sulfide is not precipitated by H_2S in a moderately acid solution. It is precipitated, along with the sulfides of iron, cobalt, nickel, and manganese, and with the hydroxides of chromium and aluminum, by H_2S in an alkaline solution, or in a neutral solution by $(NH_4)_2S$.

(2) The sulfides and hydroxides mentioned above are converted into chlorides and then into hydroxides. The hydroxides of chromium, aluminum, and zinc are soluble in an excess of $NaOH$, because of their amphoteric character. Chromium is removed by converting it into sodium chromate, and precipitating the chromate as $BaCrO_4$. Aluminum and zinc are separated by adding HNO_3 , which forms $Al(NO_3)_3$ and $Zn(NO_3)_2$, and then adding a moderate excess of NH_4OH . The aluminum is precipitated as the hydroxide, $Al(OH)_3$, and the zinc passes into solution as the complex ion, $Zn(NH_3)_4^{++}$. From this solution zinc sulfide is precipitated by H_2S in the final step of the analysis. Since ZnS is the only sulfide of the common metals which forms a white precipitate, the formation of such a precipitate in the final step of the analysis may be regarded as evidence of the presence of zinc ion in the solution.

CADMIUM

Cadmium occurs as the sulfide, CdS , in the mineral called *greenockite*. This mineral is rare, however, and the cadmium which is produced comes entirely from zinc ores. Almost all of the ores of zinc, and especially the sulfide and carbonate ores, contain some cadmium. The ratio of zinc to cadmium in these ores is about 200 to 1. During the reduction of zinc oxide, metallic cadmium is also produced and distills over with the zinc. Since cadmium is the more easily reduced, and also is the more volatile of the two metals, the first of the zinc to be condensed contains most of the cadmium. If the first portion of the distilled zinc is redistilled, and if this process of fractional distillation is repeated a number of times, the cadmium can be recovered in a fairly pure form. It can

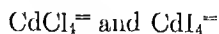
also be separated from zinc during the refining of the latter by electrolytic methods. Cadmium does not pass into solution as readily as zinc and can be precipitated along with the less active metals that are also present as impurities in the zinc. The largest portion of the commercial production of cadmium, amounting to about 2200 tons per year in the United States, is obtained in this manner.

31. Properties and Uses

Cadmium greatly resembles zinc. It is silver-white with a slight tinge of blue. It is softer, more ductile, and more malleable than zinc. It becomes brittle when heated. The metal is used in electroplating iron and steel articles, such as wire, tools, and automobile parts, to protect them against rusting. It appears to be better suited for this purpose than zinc and is used also to some extent in place of nickel. It is used to plate articles that are later plated with silver. It is also used in some anti-friction metals, in certain solders, and in several alloys of low melting point (page 527). Alloyed with silver it seems to retard tarnishing. Its alloy with gold has a greenish tinge.

32. Chemical Properties and Compounds

Cadmium oxide is brown. It is produced by the same methods as zinc oxide. With water the oxide forms the hydroxide, $Cd(OH)_2$, which is more basic in nature than zinc hydroxide. It does not act as an amphoteric hydroxide toward solutions of strong bases, although potassium cadmate, K_2CdO_2 , is produced when the oxide is fused with potassium hydroxide. The hydroxide dissolves in an excess of ammonium hydroxide to form $Cd(NH_4)_4(OH)_2$. Cadmium also forms a complex cyanide ion, $Cd(CN)_4^{--}$, and complex halide ions,



Although there are indications of the temporary existence of unstable cadmous compounds, such as $CdCl$, all the stable and familiar compounds of cadmium are those in

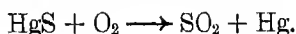
which the metal has a valence of positive 2. The chloride crystallizes from solutions as the hydrate $(2 \text{ CdCl}_2) \cdot 5 \text{ H}_2\text{O}$, and the sulfate as $(3 \text{ CdSO}_4) \cdot 8 \text{ H}_2\text{O}$. The sulfate and also metallic cadmium are used in manufacturing standard electrochemical cells for use in scientific work. The sulfide, CdS , is used as a yellow paint pigment. It is less soluble than zinc sulfide and is usually precipitated in analytical procedures with the copper group (page 460) in a moderately acid solution.

MERCURY

Mercury was known before the beginning of the Christian era. It was an important substance in the practices of the alchemists. It is sometimes called *quicksilver*. Its principal ore is *cinnabar*, HgS , but it also occurs in the native state and as amalgams of silver and gold. The chief producing localities of the world are located in Italy, Spain, California, and Oregon. The total annual production is about 4000 tons.

33. Metallurgy

The ores of mercury are of low quality and must be concentrated by flotation. The concentrate is then roasted in the air. The sulfur of the ore is converted into sulfur dioxide and the mercury is set free



Mercuric oxide does not form, because it decomposes upon heating. Since mercury is volatile, it distills as rapidly as it is produced, and the vapor is easily condensed. The metal is purified, first by filtering it through chamois skin or soft leather, and then by washing it in a dilute solution of nitric acid or mercurous nitrate. The mercury is made to flow in a fine stream through the solution of the acid. This treatment oxidizes most of the metals present as impurities and changes them into soluble compounds. Mercury is also refined by distillation under reduced pressure.

34. Properties and Uses

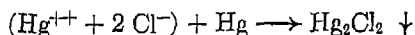
Mercury is a silver-white, liquid metal with a freezing point of -38.9° and a boiling point of 357° . It is sometimes called *quicksilver* — silver because it has the color of that metal, and quick because it moves, or "is alive." It is an excellent conductor of electricity. With many metals it forms alloys called *amalgams*. Its use in recovering gold by forming an amalgam with that metal has already been described (page 684). Sodium amalgam, which is much less active than sodium itself, is often used as a reducing agent. The amalgams of silver, gold, and tin are used in making dental fillings. Its liquid state, high density, and low vapor tension fit it for use in barometers, thermometers, and similar instruments. Since mercury has a much higher boiling point than water, it may be used advantageously instead of water in the boilers of ordinary heat engines. The great difference between the temperature of the mercury vapor and the condenser increases the efficiency with which heat is changed into mechanical energy. The use of mercury for this purpose is restricted, of course, by its scarcity.

Mercury vapor does not conduct the electric current when it is cold, but it does conduct when the vapor is heated by producing an arc in the tube containing the vapor. The tube is filled with light rich in ultraviolet radiation. If the tube is made of silica (quartz), the ultraviolet rays are transmitted through the walls and may be used in treating certain diseases and as illumination in photographic work. Mercury vapor lamps are also used as a source of light in factories and in street signs. A mercury vapor tube containing one iron electrode and one of mercury, acts as a current rectifier. This device causes the current to be conducted in one direction only and consequently is used to change an alternating current (A C) into a direct current (D C).

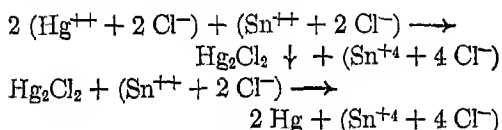
35. Chemical Properties

Mercury lies toward the bottom of the

electrochemical series and is displaced from its compounds by most of the metals. Corresponding to its position in the electrochemical series, mercury does not combine readily with oxygen, and does not displace hydrogen from acids. Like copper, it dissolves in oxidizing acids, such as HNO_3 , to form salts. The element forms two series of compounds. In one of these it has a valence of positive 1, and in the other a valence of positive 2. These are called *mercurous* and *mercuric* compounds, respectively. Both series of compounds are fairly stable under ordinary conditions, but most of the compounds of mercury decompose to form free mercury at high temperatures. Mercuric ion is easily reduced by metallic mercury to mercurous ion.



Reducing agents, such as stannous chloride, usually reduce mercuric ion to mercurous ion, and if an excess of the reducing agent is used, finally to free mercury.



This reaction is used frequently in the detection of mercury in analytical chemistry. Active oxidizing agents, such as chlorine, bromine, and concentrated nitric acid, are required to oxidize mercury or mercurous ion to mercuric ion.

Mercuric salts appear, by conductivity measurements and otherwise, to be only slightly ionized in solution. This is true, also, of the salts of zinc and cadmium. This behavior is attributed to the tendency of these salts to form complex ions, such as $\text{CdCl}_4^{=}$ and $\text{HgCl}_4^{=}$.

Mercurous compounds are usually represented by double formulas, e.g., Hg_2Cl_2 instead of HgCl . There is good reason for this practice, since in the solutions of these compounds, and in the solid and gaseous forms as well, two mercurous ions appear to be associated to form the ion, Hg_2^{++} . The mercury atom contains two electrons in the

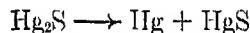
valence shell, and the shell next to this contains eighteen electrons. In the mercurous ion the valence shell still contains an electron, which is in a more or less unstable state. Greater stability is attained when two mercurous ions share their odd electrons (Hg Hg^{++}).

36 Mercurous Compounds

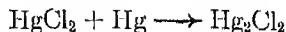
Mercurous oxide, Hg_2O , is produced when a mercurous salt is treated with an alkali, such as NaOH . It is not a stable substance. At ordinary temperatures it decomposes slowly, and at 100° it decomposes rapidly. The decomposition produces free mercury and mercuric oxide.



Mercurous oxide is not amphoteric as shown by its failure to dissolve in an excess of NaOH . *Mercurous sulfide*, Hg_2S , resembles the oxide. It decomposes under ordinary conditions into free mercury and mercuric sulfide.



Mercurous chloride, Hg_2Cl_2 , is the most important salt of the mercurous ion. Since it is only slightly soluble, it may be made by adding a soluble chloride to a solution of mercurous nitrate. It is also prepared by heating mercuric chloride with free mercury.



This reaction is reversible, and the reverse reaction is accelerated in sunlight. Mercurous chloride is a white, crystalline salt, it is only slightly soluble in water, and it sublimates when it is heated. It is the substance known in medicine as *calomel*, its medical use depends upon the stimulating effect that it has upon the liver and the organs of secretion. The medical use of calomel is safe, although the mercurous ion is very poisonous, because of the very slight solubility of the compound. Calomel should be stored in dark bottles, because it is converted in the light into the very poisonous and more soluble mercuric chloride.

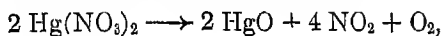
Mercurous bromide and *mercurous iodide* resemble the chloride. They are only slightly

soluble and not very stable. The iodide is the least stable of the mercurous halides.

Mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$, and *mercurous sulfate*, Hg_2SO_4 , are prepared by the action of dilute nitric or sulfuric acid upon an excess of mercury. If hot, concentrated acids are used, the mercuric salts are formed. Mercurous nitrate is fairly soluble in water, but the sulfate is only slightly soluble. Both salts hydrolyze to form basic salts such as $\text{Hg}_2(\text{OH})\text{NO}_3$.

37. Mercuric Compounds

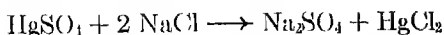
When a solution of a base is added to a cold solution of a mercuric salt, a yellow precipitate of *mercuric oxide*, HgO , is formed instead of mercuric hydroxide, which decomposes immediately even at ordinary temperatures. If the yellow mercuric oxide is heated, it changes into a red variety of the same compound. The red form is prepared directly by heating mercuric nitrate:



or by heating mercury in air. The red and yellow colors of the oxide appear to be due to differences in the state of division of the substance rather than to different crystal structures. When it is heated, mercuric oxide decomposes into mercury and oxygen. It is slightly soluble in solutions of NaOH or KOH , because of weakly acid properties.

38. Mercuric Chloride

This substance is often called *bichloride of mercury* and *corrosive sublimate*. It is produced by heating mercury in an atmosphere of chlorine, or by heating a mixture of sodium chloride and mercuric sulfate:

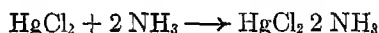


The mercuric chloride is easily recovered in a fairly pure state because it sublimes from this mixture. It is only moderately soluble in water and the solution, which is a weak conductor, appears to contain the complex compound Hg_2HgCl_4 . It is very poisonous, because it destroys the cells of the kidneys.

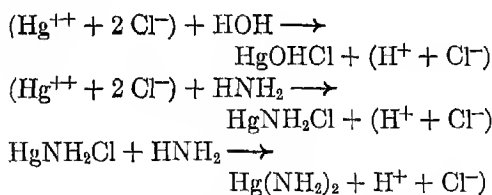
The "whites" of eggs are used as an antidote, because mercuric chloride reacts with albumen to form a precipitate. Its poisonous action involves similar reactions with the proteins of the cells. A dilute solution of mercuric chloride (about 1 part in 1000) is widely used as an antiseptic. The fluoride, bromide, and iodide resemble the chloride, the order of solubility is iodide, bromide, chloride, fluoride (most soluble). The iodide, HgI_2 , exists in two forms, scarlet and yellow. The yellow form is stable above 128° . Mercuric iodide dissolves in an excess of KI to form the complex, K_2HgI_4 . A solution of this complex and KOH , called *Nessler's reagent*, is used in detecting and estimating ammonia in various solutions and in water supplies.

39. Ammonia Compounds

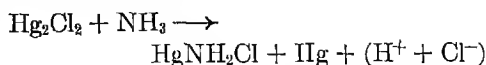
Ammonia combines with mercuric salts to form compounds which are analogous to the hydrates:



It also reacts with mercuric salts in a manner that resembles the reaction of water in hydrolysis:



A reaction of this kind, involving ammonia instead of water, is called *ammonolysis*, and the products of the reaction are an acid (HCl) and an *ammonio base* or an *ammonio-basus salt*, (HgNH_2Cl) . Mercurous chloride forms the same ammonio basic salt as mercuric chloride and liberates free mercury, when it is treated with ammonia:



The ammonio salt is white, but, because of the presence of free mercury, the precipitate

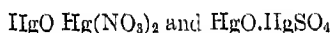
is gray or black in color. This reaction is frequently used in the detection of mercury in its univalent (mercurous) state

40. Mercuric Sulfide

As precipitated by passing hydrogen sulfide into a solution of a mercuric salt, mercuric sulfide is a black, amorphous, very nearly insoluble substance. A red crystalline form of the sulfide is made by heating a mixture of mercury and sulfur, or by grinding the two elements together and adding a warm solution of potassium sulfide. This red form, called *vermilion*, is used as a paint pigment. Mercuric sulfide is slightly soluble in solutions of sodium or potassium sulfide.

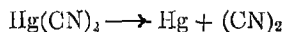
41. Other Mercuric Salts

Mercuric sulfate and *mercuric nitrate* are prepared by oxidizing the metal with hot concentrated acids. Both dissolve in water but are hydrolyzed strongly to form slightly soluble basic salts,



Mercuric fulminate is $\text{Hg}(\text{OCN})_2$. It is very explosive and is used in percussion caps to detonate other explosives, such as dynamite and the smokeless powder contained in cartridges or "shells" of shot guns, rifles, and pistols. It is made by dissolving mercury in hot nitric acid and adding alcohol.

Mercuric cyanide, $\text{Hg}(\text{CN})_2$, is soluble in water and in solutions of alkali cyanides, in which it forms the complex ion $\text{Hg}(\text{CN})_4^{2-}$. The solid salt decomposes, when heated, into mercury and cyanogen



SUMMARY

The metals of the B division of group two are distinctly different from the metals of the A division of the group, but the differences are not so pronounced as they are in group one. Furthermore, the first two elements of group two (beryllium and magnesium) resemble the elements of the B division as closely as they resemble those of

the A division. This is not true in group one. Mercury resembles the other elements in the group very little; it is more like the noble metals of group one as regards its position in the electrochemical series and the ease with which its compounds are decomposed and its ions are reduced. Zinc and cadmium lie above hydrogen in the electrochemical series, but they are not as strongly electropositive as calcium, strontium, and barium. Their hydroxides are stable but are not so strongly basic as those of calcium, strontium, and barium. Zinc hydroxide is amphoteric and, in its acidic rôle, resembles the hydroxide of beryllium. In their action upon water, zinc, cadmium, and mercury resemble beryllium and magnesium more than the metals of the A division.

Ca, Sr, Ba liberate hydrogen from cold water.
Mg liberates hydrogen from steam.

Zn and Cd, when heated, liberate hydrogen from steam.

Be and Hg do not liberate hydrogen from water or steam.

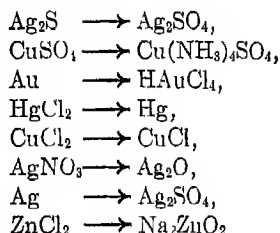
All the elements in the group have a positive valence of two. Mercury resembles copper, silver, and gold in forming, also, a series of compounds in which its valence is 1. Cadmium also acts as a monovalent metal in a few rare compounds. Zinc, cadmium, and mercury differ especially from the other members of the group in their tendency to form complex ions.

Review Exercises

1. Outline the steps involved in the metallurgy of the sulfide ores of copper.
2. Explain the principles involved in the separation of copper from gold, silver, and lead by the electrolytic refining process.
3. Explain the reactions used in the separation of gold from other metals by means of sulfure acid (page 684).
4. Suggest a method for determining the percentage of silver in a silver coin.
5. Write equations showing the different states of equilibrium which are set up when solid

silver chloride is mixed with water and ammonium hydroxide is added

- 6 Name the respects in which copper, silver, and gold differ from the alkali metals
- 7 Describe the chemical reactions involved in the metallurgy of gold (a) by amalgamation, (b) by the use of cyanides, and (c) by chlorination
- 8 Starting with a piece of solid gold and a ring made of copper, how would you electroplate the ring with the gold?
- 9 From their atomic structures explain the valences of copper and gold. Why do the alkali metals have no valence other than positive 1?
- 10 How would you bring about the following transformations?



- 11 Compare the properties of gold, silver, and copper
- 12 Describe the chemical reactions involved in Parke's process for the production of silver
- 13 Why does pure zinc dissolve more slowly in dilute sulfuric acid than the impure commercial product?
- 14 Using the principles of the solubility product and ionic equilibria explain why CdS , CuS , and HgS can be precipitated by H_2S in a dilute hydrochloric acid solution, while ZnS is not precipitated under the same conditions
- 15 Briefly outline the occurrences, metallurgy, properties, and uses of zinc, cadmium, and mercury
- 16 Give methods that could be used in preparing the following compounds and state one use for each substance: Hg_2Cl_2 , CdS , ZnO , HgCl_2 , HgS
- 17 Write a balanced equation to show the precipitation of silver from a solution of potassium argenticyanide ($\text{KAg}(\text{CN})_2$) by metallic zinc

- 18 Why is a solution of mercurous nitrate suitable for use in removing many of the metals that occur as impurities in mercury?
- 19 What is the weight of gold in an 18-carat ring that weighs 20 g?
- 20 A portion of a silver coin was dissolved in nitric acid and the silver was precipitated as silver chloride. The dried precipitate weighed 2.734 g. What did the sample of the coin weigh?
- 21 A hydrate of cupric sulfate contains 36.04 per cent of water. What is the formula of the hydrate?
- 22 What weight of chalcopyrite is required to produce sufficient cupric oxide to oxidize 1 g. of carbon to carbon dioxide?
- 23 What is the weight of a block of copper having the dimensions, in feet, of $1\frac{1}{2} \times 1 \times 2$?

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ALUMINUM AND THE METALS OF GROUP THREE

1. Introduction

Group three contains twenty-three elements, but only two of these (boron and aluminum) are very well known. The others are very rare and, for the most part, not very important as judged by their uses or the uses of their compounds. Boron has been described in a preceding chapter. It is strictly non-metallic in nature. Aluminum, which is by far the most important element of the group, is amphoteric. So, too, are gallium and indium, but they are less acidic than aluminum and boron. The others are metallic and basic. The group contains fourteen very rare elements that closely resemble one another, these are the *rare earth metals*, which have atomic numbers from 58 to 71. All the elements of the group have a valence of 3 and gallium, indium, and thallium form other series of compounds in which their valences are 1 or 2.

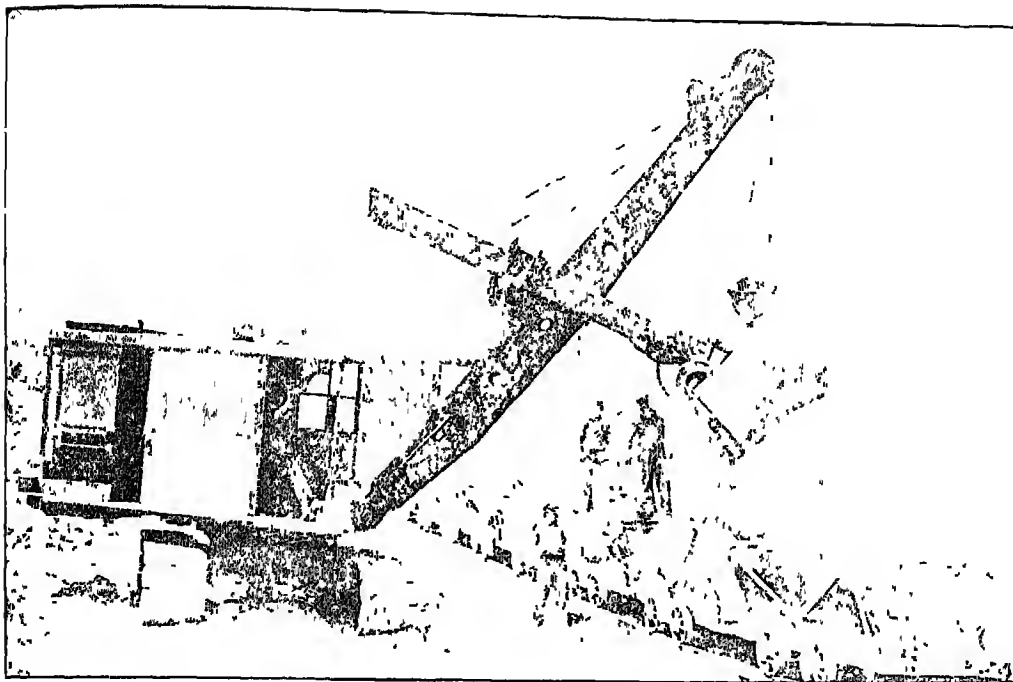
ALUMINUM

Aluminum was prepared by Oersted (1825) and Wohler (1828), who reduced aluminum chloride with metallic potassium. This was a very expensive process, and the metallic aluminum thus produced sold for about \$160 per pound. In 1854, Deville (France) produced aluminum by using sodium as a reducing agent. This led to improvements in methods of producing metallic sodium and to lowered prices for that metal. The aluminum made by Deville's process sold for about \$15 per pound. Before the world conflict began in 1939, the price was \$0.20

per pound. The metal is now produced by a process discovered in 1886 by Charles M. Hall, who began work on the problem while he was a student in Oberlin College. The name *aluminum*, as the metal was once called, or *aluminium*, as it is now called, is derived from the word *alum*. To the alchemists the term *alum* meant almost any sulfate having an astringent taste. Long before aluminum was prepared in the uncombined state, aluminum oxide was recognized as a distinct substance and was called the "base" of alum.

2 Occurrence

Aluminum is the most abundant metal and the third most abundant of the elements. Nevertheless, it is one of the latest of the metals to be produced and used on a large scale, because aluminum oxide and other compounds of the metal are not easily reduced, and because very pure compounds of aluminum must be used. Aluminum occurs most abundantly in clay, which is a hydrated aluminum silicate produced by the weathering of silicate rocks such as the feldspars (page 388). Slate and shale and many other natural silicates also contain aluminum, but none of these, except under unusual conditions, is used as a source of aluminum, because they are all difficult to reduce and contain many impurities that are not easily separated from aluminum. The most important ore of aluminum is *bauxite*, a mixture of hydrated aluminum oxide, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and non-oxide *cryolite*, Na_3AlF_6 , is also used in the production of



Courtesy of Norton Company

Figure 311 Mining Bauxite in Arkansas

aluminum Other minerals containing the element are *corundum*, Al_2O_3 , *emery*, Al_2O_3 , and the black oxide, Fe_3O_4 , of non, *garnet*, a mixed orthosilicate of non, aluminum, calcium, and magnesium, and *turquoise*, which contains a basic aluminum phosphate The oxide, with small amounts of the oxides of other metals, occurs as *ruby*, *sapphire*, *topaz*, and *oriental amethyst*

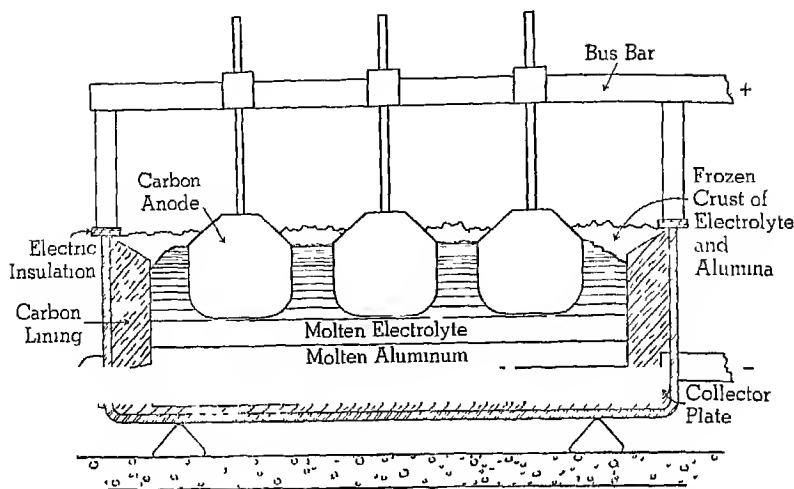
3. Metallurgy

Metallic aluminum is produced by Hall's process (see page 696), which involves the electrolysis of a solution of aluminum oxide in fused cryolite The cryolite was once obtained almost entirely from Greenland, but most of it is now manufactured Bauxite, from which the oxide is produced, comes from Arkansas and Georgia or from South America

Electrolysis is carried out in an iron tank The inside walls of the tank are coated with a mixture of coke and tar, which is carbonized more or less completely by baking, thus

giving the walls of the tank a lining of carbon This lining serves as the cathode of the cell The anodes are carbon rods (Figure 312), which are lowered until they touch the bottom of the tank An arc is thus produced, and this liberates sufficient heat to melt the cryolite, which is added at this point of the process When the cryolite has melted, the aluminum oxide is then added, and the anodes are raised Further additions of the oxide are made as electrolysis proceeds Oxygen is liberated at the anode The aluminum liberated at the cathode is in the liquid state, since the cell is operated at a temperature above its melting point (660°) It is drawn off from the bottom of the cell

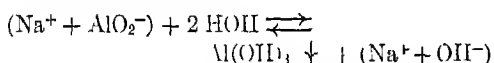
The production of aluminum is moderately expensive, partly because of the electrical energy that must be used and, also because separation of the aluminum oxide from the impurities in the natural bauxite is a rather expensive process. Very pure aluminum oxide must be used in the electrolytic cell, since the commercial refining of aluminum made from impure material is too



Courtesy of Aluminum Company of America

Figure 312 The Electrolytic Preparation of Aluminum

costly to be practical in the preparation of aluminum for ordinary purposes. Iron, especially, must be separated before the aluminum oxide is used. To obtain the pure oxide that must be used in electrolysis, bauxite is pulverized and heated with a solution of sodium hydroxide, which converts the oxide of aluminum into soluble sodium aluminate, NaAlO_2 , while the oxide of iron is left behind undissolved. After filtration, the solution of sodium aluminate is heated, and carbon dioxide is passed into it in order to neutralize some of the sodium hydroxide. Sodium aluminate hydrolyzes



The precipitate of aluminum hydroxide is recovered by filtration and heated strongly, water is expelled and pure aluminum oxide is produced.

The aluminum made by this process is more than 99 per cent pure. Aluminum was first produced in significant quantities during the last decade of the nineteenth century. In 1900, the United States produced about 7,000,000 pounds. Before 1940, the production was about 145,000 tons annually. During World War II, the production program called for 1,000,000 tons of aluminum per annum.

4. Refining of Aluminum

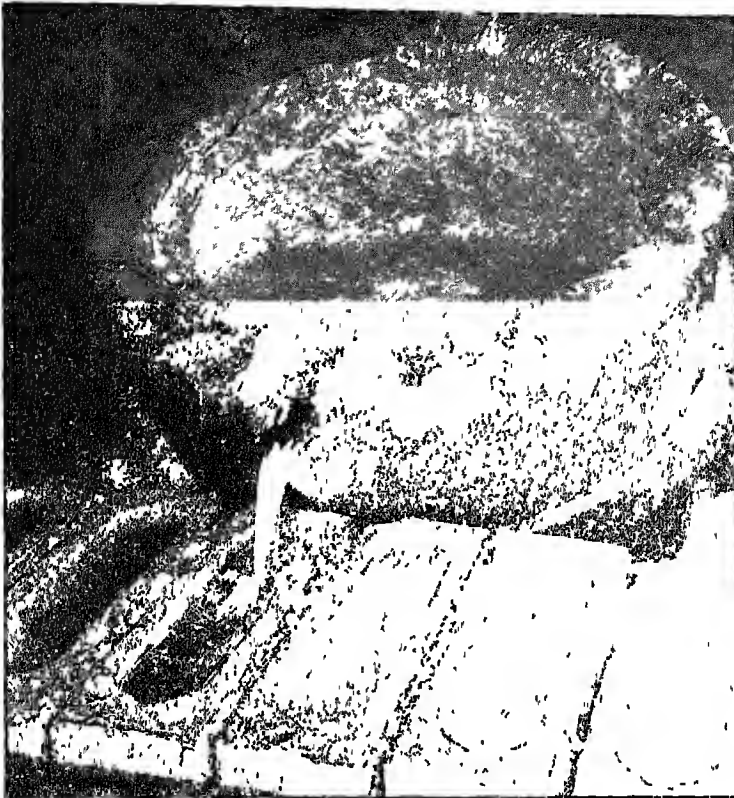
The purity of aluminum is increased from

about 99 per cent to 99.98 per cent by the Hoopes process of electrolytic purification. The impure aluminum or an alloy of copper and ordinary commercial aluminum is melted in the bottom of the cell. On top of this, there is a layer of a fused mixture of aluminum, sodium, and barium fluorides, in which aluminum oxide is dissolved. The top layer consists of fused, pure aluminum. The bottom layer is the anode and the top layer is the cathode. During electrolysis the aluminum in the bottom layer dissolves in the melted salts of the middle layer. The copper and other elements present as impurities in commercial aluminum do not dissolve. Hence, only aluminum is liberated at the cathode. This is poured off as it accumulates. Graphite electrodes dip into the upper layer, and others protrude through the walls of the cell into the bottom layer. Through these electrodes connections are made with the electrical current.

This very pure aluminum is used in making alloys. It is also used to make the so-called *Alclad* sheets, which are sheets of duralumin coated with refined aluminum. The sheets are much more resistant to corrosion than untreated duralumin. Protected in this manner, this alloy has very extensive uses in airplanes, automobiles, and in other situations where the structure is exposed to the atmosphere.

5 Physical Properties and Uses

Aluminum becomes very brittle when

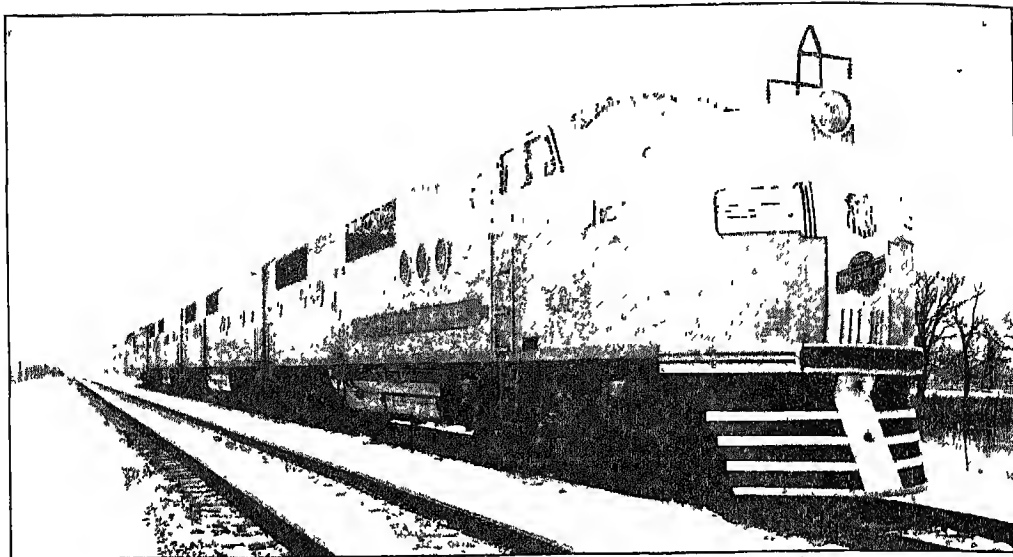


Courtesy of Aluminum Company of America

Figure 313 Pouring Aluminum Pigs from a Large Ladle

heated to 150° or higher, but at lower temperatures it is ductile and malleable. It melts at 660° and boils at 1800° . It has a high tensile strength and can be hardened by cold-rolling or drawing. The metal is not easy to solder or to cast, and it tends to adhere to tools used in machining it. It is a good conductor of heat and of electricity. As an electrical conductor its specific conductivity is not so high as that of copper, but its lower density makes it more desirable than copper for electrical power transmission cables, and weight for weight, it is the better conductor of the two. It alloys readily with many metals, such as copper, iron, magnesium, nickel, tin, and zinc. Its freshly exposed surface is silvery white in color, but the metal soon becomes covered with a thin, tenacious coat of the oxide, which produces a dull white luster.

The uses of aluminum depend upon the low density, high tensile strength, and durability of the metal or its alloys. It is used as a structural material in the construction of automobiles, railway cars, airplanes, street cars, furniture, and even buildings. Its most familiar use is in kitchen utensils. Thin sheets of aluminum are used, in place of tin foil, as a wrapping for foods and other products, in electrical condensers, as an insulator to reflect heat, in mirrors, as tinsel, and for many other purposes. Flashlight bulbs may contain aluminum foil, which is ignited by an electric current. Powdered aluminum is mixed with oil to make "silver paint." Aluminum wire and cable, also aluminum-covered steel cable, are used in constructing transmission lines. Aluminum is used to remove the oxygen from iron and steel, thus preventing the formation of blow-



Courtesy of Aluminum Company of America

Figure 314 An All-Aluminum Streamlined Train of the Union Pacific Railroad

holes in the castings. Mixed with ammonium nitrate, it makes a high explosive. It is also used in the thermit process (page 645) of welding and reducing the oxides of the metals. A rectifier (page 691) of the electric current can be made by suspending a plate of aluminum and one of iron in a solution of sodium hydroxide.

Two of the important alloys of aluminum are *magnalium* and *duralumin*. The former contains about 10 to 30 per cent of magnesium, and the latter contains about 4 per cent of copper and about 1 per cent each of manganese and magnesium. These alloys have a tensile strength about twice that of aluminum itself, and at the same time they are very light metals. Other aluminum alloys contain small percentages of other metals, such as zinc and nickel. Some of these alloys may be cast and machined. Because of their lightness and strength they are used extensively in making crank cases and other parts of the automobile where these properties are required.

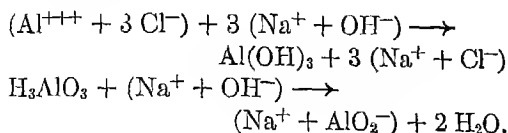
6 Chemical Properties

Aluminum reacts with the oxygen of the

air, at ordinary temperatures, only until a covering of the oxide is produced. At 600° and higher, oxidation is still somewhat slow, except in the case of the very fine powder, but at high temperatures, the metal burns with a very brilliant flame. It does not decompose water, although it is relatively an active metal, because of the deposition of the oxide or hydroxide upon the surface. It dissolves readily in hydrochloric acid, somewhat less readily in dilute sulfuric acid, and is passive or inactive toward nitric acid, which may be shipped in aluminum containers. The dissolving of the metal in nitric acid is accelerated by the presence of salts of mercury. Aluminum dissolves, also, in concentrated solutions of bases, such as sodium and potassium hydroxide, liberating hydrogen and forming aluminates (page 701). This behavior indicates the amphoteric character of the metal. Aluminum combines directly with sulfur, nitrogen, carbon, and the halogens, when it is heated in their presence. Aluminum has only a valence of positive 3. Its ordinary compounds are either aluminum salts, such as $\text{Al}_2(\text{SO}_4)_3$, or aluminates, such as Na_3AlO_3 .

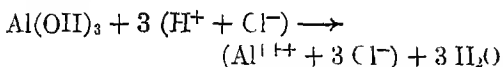
7 Aluminum Oxide and Aluminum Hydroxide

Aluminum hydroxide, $\text{Al}(\text{OH})_3$, is most easily prepared by adding a moderate amount of an alkali to a solution of an aluminum salt. If an excess of the base is added, aluminum hydroxide fails to precipitate, because it reacts as an acid, H_3AlO_3 or HAlO_2 , with the base



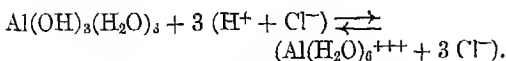
In the presence of only a moderate excess of the base aluminum hydroxide forms a white, gelatinous precipitate, which tends to become colloiddally dispersed

Aluminum hydroxide acts as a base with acids



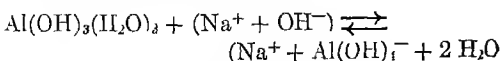
It is, therefore, to be classed among the amphoteric hydroxides

The precipitate that forms when a soluble hydroxide is added to a solution containing aluminum ion is probably the hydrous oxide, rather than the hydroxide, $\text{Al}(\text{OH})_3$. It is frequently assigned the formula $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3$, in which aluminum has a co-ordination number of 6. This substance reacts as a base with an acid, such as hydrochloric



This equation shows the aluminum ion in a solution of aluminum chloride as the hydrated ion, $\text{Al}(\text{H}_2\text{O})_6^{+++}$

As an acid the hydrated hydroxide reacts with sodium hydroxide as follows

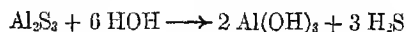


The product $\text{NaAl}(\text{OH})_4$ is sodium aluminate and is equivalent to $\text{NaAlO}_2 \cdot 2 \text{H}_2\text{O}$

When heated, the aluminum hydroxide, which is precipitated from solutions of aluminum salts, loses some of the water that

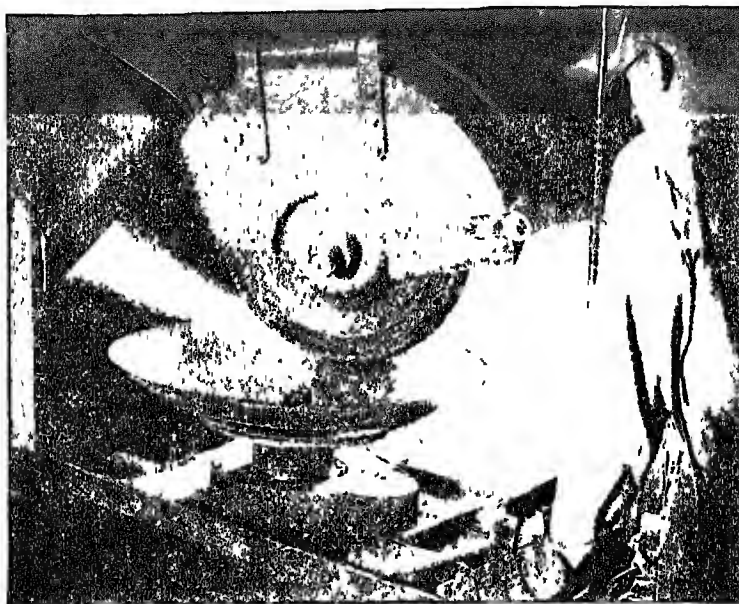
it contains and becomes $\text{HAlO}_2(\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O})$. Most of the aluminates are salts of this acid (meta aluminic acid). When the hydroxide is more strongly heated, all of the water is expelled, and the anhydride, Al_2O_3 , is formed

The salts of aluminum hydroxide and the weak acids are hydrolyzed very strongly. Such salts as aluminum sulfide, Al_2S_3 , exist only in the dry state. If the sulfide is made by the direct combination of aluminum and sulfur, and the salt is then placed in water, it is converted completely into hydrogen sulfide and aluminum hydroxide



In a similar manner the carbonate, acetate, and other salts of weak acids are hydrolyzed and form precipitates of aluminum hydroxide, when they are dissolved in water. This behavior of aluminum salts has many useful applications. Cloth which is soaked in a solution of aluminum acetate becomes impregnated with the precipitated aluminum hydroxide produced by hydrolysis. This precipitate fills the spaces between the threads, renders the fabric more nearly water-proof, and gives it a smooth and nonabsorbent surface. It may be used, also, as a mordant, since it adsorbs the dye-stuff and holds it fast in the cloth. Paper may be sized in a similar manner. The precipitated hydroxide gives a surface to the paper which is less absorbent and smoother, and which carries ink in a more satisfactory way than unsized paper. The use of aluminum sulfate in the purification of water has been mentioned in another chapter (page 179). This use also depends upon the hydrolysis of an aluminum salt. Since sulfuric acid is a strong acid, the hydrolysis is not very pronounced unless the water is alkaline. If the water is acid, sodium carbonate may be added to make it alkaline. The purification of the water depends upon the adsorbent action of the aluminum hydroxide, which adsorbs and carries down with it coloring material, colloiddally dispersed particles of clay, and even bacteria.

Activated alumina is made by strongly heating the hydroxide. It is used as a drying agent. The oxide produced by strongly igniting the precipitated hydroxide or bauxite in an electric furnace until a portion of the material fuses is hard and insoluble in acids and bases. This product is known under



Courtesy of Norton Company

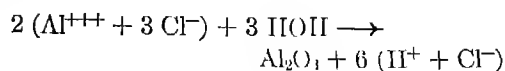
Figure 315 Polishing Cultivator Discs with a Wheel Coated with an Aluminum Oxide Abrasive, Alundum

several trade names, e g, *Alundum*. It can be ground to a powder and used to make abrasives and as a refractory (fire-resisting brick). Very hard, crystalline forms of aluminum oxide occur in nature. One of these, *corundum*, is essentially aluminum oxide and the other, called *emery*, contains magnetite in addition to Al_2O_3 . Both are used as abrasives in grinding and polishing tools and many parts of machines, such as the valves and piston rings of automobile engines. Impure, crystalline corundum also occurs naturally as some of the most valuable gems. Ruby is corundum containing the oxide of chromium, Cr_2O_3 . The blue sapphire contains the oxides of titanium, iron, cobalt, and chromium. Artificial rubies and sapphires are now produced in quantities that run into the millions of carats. These have approximately the same composition and appearance as the natural stones, but may be distinguished from them by certain characteristics of the tiny bubbles that appear in the stones; those in the natural gems are round, while those in the artificial ones

are flattened. The imitations found in very cheap jewelry are merely red or blue glass.

8. Aluminum Chloride, AlCl_3

Anhydrous aluminum chloride is made by the direct action of chlorine upon aluminum. The principal commercial process, however, involves the action of chlorine upon bauxite mixed with coal. If metallic aluminum or aluminum hydroxide is treated with hydrochloric acid, a solution of aluminum chloride is produced. When this solution is evaporated, crystals of the hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, are formed, but the anhydrous salt cannot be obtained by complete evaporation and heating to expel the water of hydration. Instead, the salt hydrolyzes and forms the oxide and hydrochloric acid



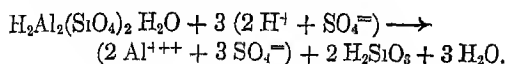
Anhydrous aluminum chloride is purified by sublimation. It combines with water very readily and is used as a reagent and as

a catalyst in many organic reactions. One of the processes used in cracking petroleum oils, for example, employs aluminum chloride as the catalyst.

The iodide, bromide, and fluoride resemble the chloride of aluminum. The fluoride forms complex salts, of which cryolite, Na_3AlF_6 , is an example. All of the halides form compounds resembling hydrates with ammonia ($\text{AlCl}_3 \cdot 6 \text{NH}_3$).

9. Aluminum Sulfate $\text{Al}_2(\text{SO}_4)_3$

Aluminum sulfate is prepared by treating bauxite or clay with sulfuric acid. With clay the acid reacts as follows:

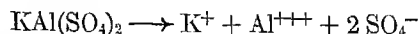


The aluminum sulfate is recovered by filtering the solution, in which the silicic acid is insoluble. The filtrate is then evaporated and crystals of $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ are formed. This substance is now largely used for most of the purposes formerly served by *alum*.

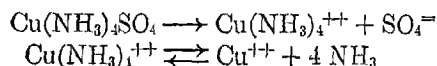
Alum is the term which is most often used in referring to the *double salt* $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$. It is made by mixing potassium sulfate and aluminum sulfate in equal molecular proportions, and dissolving them in water. The solution is then allowed to evaporate, and crystals of alum are formed. Other alums may be made in a similar manner. Instead of potassium sulfate, the sulfate of ammonium, of another alkali metal, or of other univalent metals, such as silver or thallium, may be used. Aluminum may be replaced by chromium, iron, manganese, or other elements that have a positive valence of 3. As an example of one of these alums, we may mention the double salt of cesium sulfate and ferric sulfate, $\text{CsFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$. This is cesium iron alum. All the alums form crystals of the same system—they have the same shape or form, one alum can be deposited from solution upon the surface of the crystals of another alum without change in crystal form or structure. Using M and M' to denote a univalent and a tri-

valent metal, respectively, the general formula for an alum is $\text{M}_2\text{SO}_4 \cdot \text{M}'_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$ or $\text{MM}'(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$.

The alums are called double salts. They should be distinguished from compounds containing complex ions. The former ionize in solution to form only simple positive and negative ions.



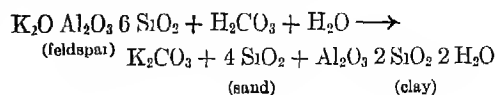
The latter yield at least one complex ion, which may ionize further, but usually only to a slight extent, to form simple ions or neutral molecules.



Alum and aluminum sulfate are used in fire extinguishers (page 306), in baking powders (page 384), in purifying water (page 179), with rosin in sizing paper, and in the photographic fixing bath to harden the gelatin. These uses depend upon the hydrolysis of the aluminum salt. In baking powders, the acid which is formed by this reaction is the important substance. This is true, also, in certain fire extinguishers. In extinguishers of the foam-producing type and in the purification of water, the formation of aluminum hydroxide is important.

10. Aluminum Silicates, Ceramics

Many of the most important silicate rocks contain aluminum (page 534). The weathering of these rocks results in the disintegration of the complex silicates which they contain. The effect of the weather is due to the thawing and freezing of water in the rocks, and to the action of water and carbon dioxide as chemical reagents. When a potassium feldspar disintegrates, potassium carbonate, which is soluble, is formed and is largely removed by water. The residue that remains is soil and consists of sand and clay.



Pure clay, which has the formula shown above, is white and is called *kaolin*. Ordinary clay contains compounds of iron and of other metals. These give it a yellow or reddish-yellow color. Clay of this kind has often been washed away from the locality where it was formed and has been deposited as sediment in some other place. Kaolin is used to make porcelain and china. These usually contain, also, some feldspar, which melts easily and serves to cement the parts of the clay article together, making of it a semi-vitrified body. Impure clays are more easily fused because of the presence of the oxides of iron, calcium, magnesium, and other metals that form easily melted silicates with sand. These clays are used to make brick, tile, and stoneware, such as crocks, jars, and jugs. The articles are buff or red in color after they have been heated in the kiln, because of the presence of ferric oxide. Stoneware is usually glazed, to give it a less porous surface, by throwing salt upon the articles while they are hot. This treatment produces sodium aluminate and sodium aluminum silicate, which melt readily and cover the entire surface. When the article cools, the covering solidifies, producing a compact, smooth, waterproof surface. China ware is made from a mixture of kaolin with bone ash and feldspar, the two latter materials fuse when heated, and fill the pores between the grains of kaolin.

The use of clay in making pottery and other ceramic articles depends upon the plasticity of the paste which is made of clay and water. When soaked in water the clay progressively hydrates, and the paste becomes more plastic. When it is heated, it loses the water of hydration, and forms a hard, rock-like mass. The dried clay has lost its plasticity and, when placed in contact with water, is not dispersed.

Preparatory to the fashioning of articles on the potter's wheel or in the mold, the finely divided clay is suspended in water. The suspension is called the *slip*. This material is stored until it is to be used. It is then separated from most of the water by means of filter presses. The clay, that comes from the presses as moist cakes, is

kneaded in machines. The kneading operation is called *pugging*. The fashioning of articles on the potter's wheel is called *jiggering*. *Pressing* is the process used to make articles such as dishes. The clay is pressed upon a plaster mold and the exterior surface is smoothed, cut, and finished by hand. The articles are placed in *saggers*, which are containers made of fire clay. The saggers are stacked in kilns, which are heated to about 1300°. Oil and gas are often used as fuels. The heating process is called *firing*. The product that has been fired once is called *bisque*. Since it is porous, it must be *glazed*, that is, the articles are coated with a paste of finely ground feldspar, and returned to the kiln for a second firing, during which the glazing materials melt to form a glass-like covering that spreads over all the surface and fills the pores between the particles of kaolin. Decorative designs may be painted upon the ware after the second firing. These designs are made by means of the oxides of different metals, which dissolve in the glaze or react with it to form colored silicates. The colors are baked in by a third firing in the kilns.

Porcelain is made of the purest clays obtainable. These are mixed with quartz and feldspar, and after grinding, the material is floated in water to remove all the coarse particles. It is then passed through filter presses, and a thick paste is obtained. This material is then stored for some time to increase the extent to which the clay is hydrated — a procedure that results in a more plastic product. The plastic mixture is then made into the desired articles either on the potter's wheel or by means of molds, and the articles are heated at a temperature of about 1250° in the firing kiln. Water is thus driven out of the clay, leaving anhydrous aluminum silicate, and the feldspar melts and dissolves the quartz. Upon cooling, therefore, the article is almost glass-like in appearance except for the presence of the insoluble aluminum silicate, which makes it opaque. After the first firing, porcelain ware is covered with a paste made of kaolin, limestone, quartz, and feldspar, and heated again.

Fire brick is made from fire clay, which does not soften until it is heated to a tem-

perature above 1500° . It resembles kaolin and is purer than ordinary clay. Brick made from this clay is used as a refractory in building glass-pots, kilns for firing porcelain, crucibles for melting metals, furnaces, and the like. The bricks are fired or baked at a high temperature and are harder, more dense, and less porous than ordinary bricks, which are made from clays containing larger percentages of impurities.

11 Ultramarine and Lapis Lazuli

Ultramarine is produced artificially by fusing a mixture of kaolin, sodium carbonate or sulfate, sulfur, and resin or some other carbonaceous material. The fused material has colors that vary with the composition and the conditions under which it is made, from red through green and violet to blue. The blue product is used as a pigment and as bluing. A similar substance occurs in nature as the very rare mineral, *lapis lazuli*. This has a very beautiful, permanent blue color. It has long been prized for its use in painting, in mosaics, and in decorations of various kinds.

12 Fuller's Earth

A very adsorbent variety of clay, called fuller's earth, is produced in the United States to the extent of almost 300,000 tons each year. The states which lead in the production are Florida, Arkansas, Texas, Georgia, Alabama, California, and Massachusetts. Fuller's earth is used as a filtering medium and decolorizing agent in the purification of oils and as a filler in soaps. It owes its name to its early use in removing the grease from wool. This process was called "fulling."

13 Gallium

When Mendeleeff constructed his periodic table of the elements he predicted the existence of an element to which he gave the name *eka-aluminum*. This prediction caused others to seek the missing element, and about four years later the prediction was fulfilled, when the spectroscope showed the existence of a new element in zinc blende. This element was named *gallium* after France

(Gallia). The metal is white and soft. It melts at about 30° , and consequently is in the liquid state in warm weather. It corrodes easily in the air. It forms some compounds in which it has a valence of 2 and other compounds in which it has a valence of 3. In its trivalent state it greatly resembles aluminum. Gallium hydroxide is amphoteric, forming gallates when it dissolves in bases and gallium salts when it reacts with acids. Examples of these are sodium gallate, NaGaO_2 , and gallium chloride, GaCl_3 . The metal is produced by electrolyzing a salt of gallium in an alkaline solution. Its compounds occur in small amounts in some of the ores of iron, zinc, aluminum, and chromium.

14. Indium

Zinc blende yielded another new element to which the name of *indium* was given. This name refers to the two blue lines of its spectrum. It occurs in small amounts in some of the ores of zinc, lead, manganese, iron, tungsten, and tin. Most of the indium which is recovered is obtained in the purification of zinc spelter. The pure element resembles gallium and aluminum. Like these metals, its usual valence is 3, but it also acts as a bivalent and as a univalent metal. Indium hydroxide, $\text{In}(\text{OH})_3$, is amphoteric, but it is not so soluble as aluminum hydroxide in bases. It reacts slightly, forming the indate ion, InO_2^- . Alloys of indium are used in jewelry, and the element itself is sometimes applied to certain metals as a coating to prevent corrosion.

15. Thallium

The name of this element comes from a Greek word which means "green budding twig." It refers to a characteristic green line in the spectrum of the element. It is found in zinc ores in which it occurs in larger amounts than gallium and indium. It is also found in iron pyrites and in minerals containing lead, tellurium, and the alkali

metals. It is recovered from the dust that collects in the flues of sulfuric acid plants in which sulfur dioxide is obtained by roasting pyrites. The metal has a bluish-white color, is soft and malleable, and melts at about 303° . Thallous hydroxide, $TlOH$, is moderately soluble and is strongly basic. Thallous chloride, bromide, and iodide are slightly soluble. Thallous hydroxide, $Tl(OH)_3$, is not amphoteric; it does not react with bases. With acids it forms salts such as $TlCl_3$ and $Tl(NO_3)_3$. These salts are highly hydrolyzed, partly because the hydroxide is a weak base, and also because it is very slightly soluble. Metallic thallium is used to some extent in making alloys. Thallium compounds are sometimes used in the manufacture of optical glass in order to increase the index of refraction.

16. The A Division of Group Three

The A Division of this group contains scandium, yttrium, lanthanum, and fifteen elements whose atomic numbers lie between 57 and 71. All these elements are generally included in the group which is called the *rare-earths*, although in the periodic classification this term refers only to the 14 elements immediately following lanthanum and preceding hafnium. Because of the close relationships of scandium, yttrium, and lanthanum to these elements, however, we shall consider them along with the rare-earths. The A Division also contains actinium which is best known because of its radioactive properties.

The rare-earth elements are metals in character. They resemble one another so strongly that their separation is extremely difficult, and for a long time their existence as individual elements was not recognized. The first discovery concerning these elements was made about 1800, when two oxides were found. These were called yttria and ceria. Later, it was discovered that these compounds were not simple oxides but contained all of the elements that we now call the rare-earths. The individual elements were discovered from time to time. The last one, discovered by Hopkins in 1926, was number 61 and was called illinium. Ceria was found to consist for the most part of the oxides of lanthanum, cerium, praseodymium, neodymium, illinium,

and samarium. Yttria was found to contain the oxides of yttrium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium.

The principal source of the rare-earths is *monazite* sand. This is a complex phosphate, to which the general formula MPO_4 (where M is a rare-earth metal) may be assigned. Monazite is found as an alluvial sand along the seacoast of Brazil and in India.

These metals form oxides corresponding to the general formula M_2O_3 . Cerium forms the oxide CeO_2 as well as Ce_2O_3 . There is only a slight change in properties from scandium to lutecium. Scandium resembles aluminum more closely than the others do. It is the least basic element in the entire division. Basic properties show a slight increase in prominence as the atomic weight increases. The most abundant of the rare-earths are those with even atomic numbers. The salts of many of the metals are colored red, green, pink, rose, orange, or yellow. The ions of yttrium, scandium, lanthanum, gadolinium, terbium, ytterbium, and lutecium are colorless.

The metals are produced by the electrolysis of their oxides dissolved in a bath of melted rare-earth fluorides. In the combined state they are separated from the compounds of other metals by precipitating them as oxalates in the presence of nitric acid. *Misch metal* is an alloy of the rare-earth metals; it is made by the electrolysis of a mixture of the chlorides. It is used as a pyrophoric alloy in cigarette and gas lighters, because of the ease with which it may be ignited by scratching. It may also be used to remove oxygen from cast iron, and in tracer bullets of machine guns and in luminescent shells, which show the positions of the "hits" by the light emitted when the alloy is ignited. Cerium dioxide (CeO_2) is used in making Welsbach gas mantles (page 574). For this purpose a mixture containing 1 per cent of CeO_2 and 99 per cent of thorium oxide, ThO_2 , is used. Thorium occurs with the rare-earth metals in monazite sand. Cerium dioxide is also used in analytical chemistry as a powerful oxidizing agent (in acid solution).

The similarity in the chemical behavior of these metals is explained by the similarity of their atomic structures. In the atom of the first rare-earth metal, lanthanum, the first, second, and third electron levels are filled, and the fourth level contains 18 electrons. The fifth level con-

tains 11 electrons which are divided into sub-groups of 2, 6, 1, and 2 electrons

Lanthanum		
Level 1	Level 2	Level 3
2	2-6	2-6-10
	Level 4	Level 5
	2-6-10	2-6-1-2

The outermost elections of the third and fourth sub-groups of the fifth level are not held very firmly, and their removal from the atom accounts for the valence of 3. In the other rare-earths, from lanthanum to lutetium, the additional elections are located in the fourth level, which is not filled until it contains 32 elections, and which in lanthanum, therefore, has 14 vacant electron-positions. In lutetium the last of these positions is filled, and additional elections (in hafnium, tantalum, etc.) must go into some of the sub-groups of the fifth level.

Lutetium		
Level 1	Level 2	Level 3
2	2-6	2-6-10
	Level 4	Level 5
	2-6-10-14	2-6-1-2

In all of the rare-earth metals, therefore, the outer groups of elections remain the same, and the elements consequently display the same, or very nearly the same, chemical behavior and have the same valence.

Review Exercises

1. Discuss the occurrences of aluminum in nature and describe the method by which the metal is produced.
2. Why can metallic aluminum not be prepared in the same manner as metallic copper or metallic zinc?
3. Suggest some method, consisting in a series of reactions, that might be used to produce metallic aluminum from clay. Why is this method not used as extensively as the one that starts with bauxite?
4. Write equations to show (a) the amphoteric character of aluminum hydroxide and (b) the hydrolysis of aluminum acetate.
5. Assuming an efficiency of 60 per cent, what weight of crystalline aluminum sulfate could be produced from one ton of pure kaolin?
6. What weight of pure "potash" alum could be prepared from the weight of aluminum sulfate

made from the clay (see preceding problem?)

7. What is a double salt? Give examples of double salts and salts containing complex ions, and point out the differences between them.
8. What is the general chemical composition of an alum?
9. Why does a precipitate consisting of aluminum hydroxide form when hydrogen sulfide is passed into an alkaline solution containing aluminum chloride?
10. Describe the Goldschmidt process, its uses, and the reactions which it involves.
11. Compare and contrast, in a general way, the properties of aluminum with those of each of the following: gallium, indium, thallium, and the rare-earths.
12. What is the source of the rare-earths? Account for the very close resemblance of these elements as regards their chemical properties.
13. Explain the meaning of the following: misch metal, fuller's earth, porcelain, Alundum, ferric alum, magnalium.
14. Explain the origin of clay.

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THE METALS OF GROUP FOUR

1 Introduction

Of the elements of group four, carbon, silicon, and the A elements — titanium, zirconium, and hafnium — have been discussed in earlier chapters. Four others are to be discussed in this chapter: tin, lead, germanium, and thorium. As pointed out in Chapter 34, hafnium, zirconium, and even titanium have some metallic characteristics, but properly speaking these elements are to be considered as members of the silicon family rather than the family that contains tin and lead. Like the elements of the A division, the elements of the B division have a valence of 4 in some of their compounds, a valence of 2 is also encountered in some of their compounds.

TIN

2. Occurrence

It is estimated that about 0.00001 per cent of the earth's crust is tin. The most important ore of this metal is the mineral *cassiterite*, SnO_2 , sometimes called *tin stone*. Tin was obtained from deposits of cassiterite in England by the Romans and Phoenicians. The Romans called the element *stannum*, and it is from this Latin name that our present symbol, Sn, for tin is derived. The principal deposits of cassiterite in the world today are located in the Malay States, Bolivia, the Dutch East Indies, Spain, China, England, and Australia. There are only a few deposits of the mineral in North America, and these are not important. Some tin is recovered from scrap tin plate in the United States, and during the recent war, a smelter was built in Texas for the reduction of Bo-

livian ore. The world's annual production is about 180,000 tons. In addition to its occurrence as cassiterite, tin occurs in several complex sulfides and oxides. These minerals are of little importance as a source of the element.

Cassiterite is a heavy mineral, and for this reason it is often found as gravel in the beds of streams that have removed the mineral from the deposits in which it occurred originally. A considerable portion of the tin that is recovered comes from alluvial deposits of this kind. This tin is known as "stream tin."

3 Metallurgy

Cassiterite ores are of low grade and must be concentrated before being treated for the recovery of the metal. The usual method of concentration is a flotation process, in which the heavy particles of the ore settle and the lighter, worthless portions are carried to the top in the froth. The concentrated ore is roasted to remove sulfur and arsenic or volatile oxides, and also to convert zinc, iron, and copper into their oxides. It is then washed with a solution of hydrochloric or sulfuric acid, which changes the oxides of all of the metals, except tin, into soluble chlorides or sulfates. The tin concentrate is then smelted in a reverberatory furnace with pulverized carbon (coke or hard coal), which reduces the oxide of tin to the free metal. Some of the tin remains in the slag as a silicate, and some is carried away in the dust from the furnace. Both slag and dust are smelted again. The tin set free during smelting is drawn off from the bottom of the furnace and refined by one of several

methods. It may be stirred, while molten, with green poles (page 673). It may be heated in a furnace with a sloping hearth, the tin which melts at a low temperature flows toward the bottom of the furnace, leaving slag and other less fusible materials at the top. Purification may also be accomplished by a process called "tossing." This consists in pouring the melted tin from large ladles. The impurities, which are less fusible and consequently solidify before the tin, are left in the ladles as the liquid tin is poured off. At the same time, some of the metallic impurities are readily converted to oxides by being brought into close contact with the air. The repeatedly melting and pouring of the tin removes these oxides as portions of the solid material that remains in the ladles. The purified metal is cast into large blocks and is called "block tin." More highly refined tin is obtained by electrolysis, using impure tin anodes, pure tin cathodes, and a bath of fluosilicic acid (H_2SiF_6) and sulfuric acid.

Tin is recovered from scrap tin plate, which is used in making cans, pails, and other utensils, by several methods, one of which involves the action of dry chlorine upon the tin coating of the plate. Chlorine converts the tin into stannic chloride, which is a volatile liquid, but it has little effect upon the iron that lies beneath the tin layer.

4 Properties

Tin exists in two allotropic forms, *gray tin* and *white*, or malleable, tin. The transition temperature at which one form changes into the other is 18° . The ordinary form is that of a white malleable metal, which melts at 232° and boils at 2270° . This form of tin is crystalline in structure, and the crystals slip over one another, when a rod of the metal is bent, producing a sound described as "tin cry." When cooled to 18° , white tin slowly changes to the gray form. At lower temperatures, the change is more rapid, and the speed of the transformation is increased by the presence of a small amount of gray tin

or stannous chloride. Gray tin has a cubic crystal-lattice, while white tin has a tetragonal lattice. The change to gray tin also involves an increase in volume. Both these factors result in the formation of a brittle, easily crumbled metal. Articles made of tin are consequently likely to disintegrate in cold weather. The change slowly progresses from some point of origin and produces an effect which, in a way, is similar to infection in a plant or animal body. It is called "tin disease."

5 Uses

White tin can be rolled into thin sheets, or tin-foil, which is used for wrapping foods and other products. The metal is very resistant to corrosion, and for this reason is used to make "block tin" pipes for conveying distilled water and other liquids. It is also used to coat sheets of iron, copper wire, and the like. Tin plate—used for cans, cooking vessels, and similar articles—is made by dipping sheets of iron in melted tin or by depositing tin electrolytically upon the sheets. About one third of the tin used in this country goes into tin plate. The iron is first cleaned of oxides by "pickling" (page 350). The coat of tin, which is inactive toward oxygen, protects the iron from corrosion. If any iron is exposed, or if the layer of tin is scratched through, the iron corrodes rapidly, and the tin affords no protection, since it is lower in the electrochemical series than iron. If iron and tin are in contact with each other, and if both are in contact with moist air, iron corrodes more rapidly than it does when it is alone.

Tin is also used to produce many alloys. Some of these are listed in the table below, in which the numbers in parentheses refer to the percentages of the metals present in the alloy.

Solder	Sn (50), Pb (50)
Pewter	Sn (80), Pb (20)
Type metal	Sn (5), Pb (80), Sb (15)
Rose's metal	Sn (23), Pb (27), Bi (50)

White metal, tinsel, bell metal, Britannia metal, and gun metal are other alloys that contain tin. These vary considerably, not only in the percentages of the constituent metals, but sometimes in the number of metals that they contain.

6 Chemical Properties

Tin is not attacked by air and moisture at ordinary temperatures, but at higher temperatures it is coated with a layer of oxide. When heated in the air above its melting point, it is slowly oxidized, and at high temperatures (1500°–2000°) it burns with a white flame. The metal reacts more readily with chlorine and the other halogens than it does with oxygen. Dry chlorine converts it into stannic chloride. It also combines directly with sulfur when heated with that element. It reacts only slowly with dilute hydrochloric acid to form stannous chloride, SnCl_2 , and hydrogen. It reacts more rapidly with concentrated hydrochloric acid. It also reacts slowly with dilute sulfuric acid to liberate hydrogen, but it reduces the concentrated acid, liberating sulfur dioxide. Dilute nitric acid acts upon tin to form stannous nitrate, $\text{Sn}(\text{NO}_3)_2$, and at the same time nitrogen is reduced to one of the lower oxides of nitrogen or to ammonia, which forms ammonium nitrate. Concentrated nitric acid oxidizes tin very vigorously to the insoluble beta metastannic acid, H_2SnO_3 , (better represented, perhaps, as the hydrous oxide, $\text{SnO} \cdot n\text{H}_2\text{O}$) and liberates nitric oxide or nitrogen dioxide. Tin is also attacked by hot solutions of sodium hydroxide and other alkalis, in which it dissolves, forming stannites, such as Na_2SnO_2 , and liberating hydrogen. This behavior of tin is similar to that of aluminum and zinc, and shows that stannous hydroxide is amphoteric in nature.

7 Compounds of Tin

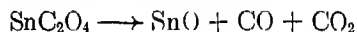
Tin has two valence numbers, 2 and 4. Acting as a metal, it forms, therefore, two series of salts, of which *stannous* chloride, SnCl_2 , and *stannic* chloride, SnCl_4 , are typi-

cal examples. The latter, however, does not show the characteristic properties of a salt to a pronounced degree; in the pure state it does not conduct the electric current, and when dissolved in water, it is highly hydrolyzed. The fact that it exists as a liquid under ordinary conditions is also contrary to the general nature of salts and reveals a relationship between stannic chloride and the chlorides of the non-metals, such as carbon tetrachloride. Stannic sulfate, $\text{Sn}(\text{SO}_4)_2$, more closely resembles the true salts than does stannic chloride.

Acting as a non-metal, or acid-forming element, tin forms two series of compounds, *stannites* and *stannates*. These compounds are salts of stannous acid ($\text{Sn}(\text{OH})_2 \rightarrow \text{H}_2\text{SnO}_2$) and stannic acid ($\text{Sn}(\text{OH})_4 \rightarrow \text{H}_4\text{SnO}_4 \rightarrow \text{H}_2\text{SnO}_3 + \text{H}_2\text{O}$), respectively.

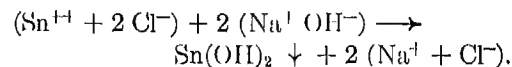
8 Stannous Oxide, SnO , and Stannous Hydroxide, $\text{Sn}(\text{OH})_2$

Stannous oxide is a black or green powder, depending upon the method of production. It is prepared by heating stannous hydroxide or stannous oxalate, SnC_2O_4 .

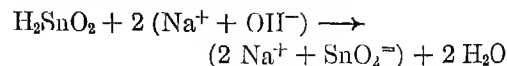


It burns in the air, when it is heated, and forms stannic oxide.

Stannous hydroxide cannot be prepared in the pure, dry state. When the precipitated hydroxide is heated, it is dehydrated, forming first $(\text{SnO})_2 \cdot \text{H}_2\text{O}$ and finally the oxide. It may be precipitated by adding an alkali hydroxide to a solution of a stannous salt.



The precipitate dissolves in an excess of the alkali, forming sodium stannite.



It also dissolves in acids, forming salts like SnCl_2 . The hydroxide, therefore, is amphoteric.

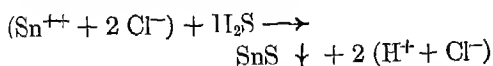
Like the corresponding compounds of zinc (page 689) and aluminum (page 701) the compound that we have represented above as stannous hydroxide, $\text{Sn}(\text{OH})_2$, is probably the hydrous oxide, $\text{SnO} \cdot n\text{H}_2\text{O}$

9 Stannous Chloride, SnCl_2

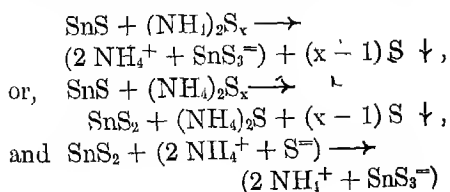
A solution of this salt can be prepared by dissolving tin in concentrated hydrochloric acid. The anhydrous salt is prepared by passing hydrogen chloride over the metal. When a solution of stannous chloride is evaporated, crystals of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ form. When heated, this hydrate liberates hydrochloric acid by the hydrolysis of SnCl_2 , which is converted into the basic salt, $\text{Sn}(\text{OH})\text{Cl}$. Stannous chloride is widely used as a reducing agent, because of the tendency of tin to pass into the quadrivalent condition. It reduces mercuric chloride to mercurous chloride (page 692) and ferric chloride to ferrous chloride. These and similar reactions are frequently employed in analytical chemistry. It is used in dyeing as a mordant, in weighting silk, and in the manufacture of tin-coated metallic articles, such as pins.

10 Stannous Sulfide, SnS , and Stannic Sulfide, SnS_2

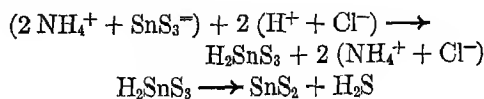
Stannous sulfide is precipitated as a dark-brown solid when hydrogen sulfide is passed into a solution of a stannous salt



The precipitate forms in the presence of a moderate excess of HCl , but is readily soluble in concentrated acid. It is not soluble in ammonium sulfide, but it does dissolve in ammonium polysulfide. It is first oxidized by this reagent to stannic sulfide, which then dissolves to form ammonium thiostannate



These reactions are important in the separation of tin from other metals whose sulfides do not react with ammonium sulfide. They show that SnS_2 , like SnO_2 , is acid-forming in character; that is, the thiostannates are salts of thiostannic acid, H_2SnS_3 , which corresponds to stannic acid, H_2SnO_3 . Thiostannic acid is not stable. Whenever it is produced by the action of acids upon its salts, it immediately decomposes, forming stannic sulfide



Stannic sulfide is a yellow solid; it can be precipitated by H_2S from solutions containing the Sn^{++} ion

11. Stannic Oxide, SnO_2

Stannic oxide is a powder which is white when cold and yellow when hot. It is prepared by burning tin or stannous oxide at a high temperature, or by igniting stannic hydroxide. If the oxide is strongly heated it becomes inactive and resembles the mineral cassiterite. If prepared at a relatively low temperature, it dissolves in acids and in alkalis. It is used in the manufacture of opaque glass and enamels.

When ammonium hydroxide is added to a solution of a stannic salt, a jelly resembling silicic acid is produced, instead of the definite compound, $\text{Sn}(\text{OH})_4$, that we might expect. This substance possesses acidic properties, it is sometimes called metastannic acid and assigned the formula H_2SnO_3 . A substance of similar composition is formed when nitric acid acts upon tin (page 710). Both substances are probably hydrous oxides which differ in water content. The compound made by precipitation is called *alpha-stannic acid* and that made by the action of nitric acid upon tin is called *beta-stannic acid*. The former dissolves readily in dilute acids and alkalis but the latter does not. Sodium metastannate, Na_2SnO_3 (or as the formula is frequently written to show the probable extent of hydration, $\text{Na}_2\text{Sn}(\text{OH})_6$), is used in fireproofing cloth and in weighting silk. Cloth to be fireproofed

is dipped in a solution of sodium stannate and then into a solution of ammonium sulfate. The latter hydrolyzes to liberate hydrogen ions, which react with stannate ions to form stannic acid. The acid is deposited in the cloth and makes it noncombustible.

Like other ions of this kind, the stannate ion probably exists in solution as the hydrated ion, $\text{SnO}_3 = 3 \text{H}_2\text{O}$ or $\text{Sn}(\text{OH})_6^-$.

12. Stannic Chloride, SnCl_4

We have already mentioned some of the unusual properties of this compound (page 710). It is made by the action of an excess of chlorine upon tin. The anhydrous compound is a liquid which boils at 114° and freezes at -30° . With water it forms a crystalline hydrate, which has the formula $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$. It forms a complex acid with hydrogen chloride, H_2SnCl_6 . This substance is called *chlorostannic acid*. The ammonium salt of this acid, $(\text{NH}_4)_2\text{SnCl}_6$, is used as a mordant in dyeing. Stannic chloride itself is used for a similar purpose and also for weighting silk. These uses depend upon the hydrolysis of the tin compounds and the formation of stannic acid. With alcohol and ammonia, stannic chloride forms compounds that are analogous to the hydrates.

LEAD

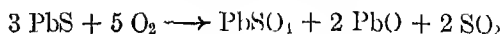
13. Occurrence

Lead was produced and used by the Egyptians, Babylonians, and Romans. The symbol, Pb, of the element comes from the Latin name *plumbum*. The most important ore of lead is *galena*, PbS , which is found in association with sulfide minerals of zinc, silver, copper, arsenic, antimony, bismuth, and tin, and with other minerals, such as quartz, fluorite, and barite. *Cerussite*, PbCO_3 , and *anglesite*, PbSO_4 , are also of some importance. The United States and Mexico produce approximately one half of the world's supply of lead. Spain, Australia, Canada, and Germany are the other principal producing countries. Most of the lead produced in the United States comes from

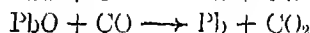
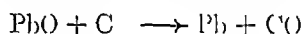
Missouri, Idaho, and Utah. The world's annual production is about 1,700,000 tons, of which the United States produces 425,000 tons.

14. Metallurgy

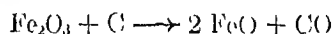
The lead ore is crushed, concentrated by flotation, and then roasted in a furnace to remove a part of the sulfur. During the roasting the sulfides of iron, zinc, and copper are changed into oxides. The lead sulfide is partially converted into lead monoxide, PbO , and lead sulfate, PbSO_4 .



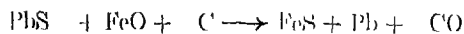
Some of the lead sulfide remains unchanged. This material is then mixed with fresh ore, iron ore (Fe_2O_3), carbon, and limestone, and heated in a small blast furnace. Au is forced in at the bottom of this furnace. The limestone is added as a flux for the silica which is present in the ore. Several reactions occur, but the principal one is the reduction of lead monoxide by carbon or carbon monoxide.



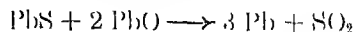
The carbon also reduces ferric oxide to ferrous oxide.



Ferrous oxide aids in the liberation of metallic lead by participating in the following reactions.



Some lead is also produced by the interaction of lead sulfide and lead oxide.



The lead is drawn off from the blast furnace as lead *bullion*. This contains some silver, gold, bismuth, zinc, copper, arsenic, antimony, and other metals. The remaining products of the furnace are the slag, which is worthless, and a *matte*, which consists of the



Courtesy of National Lead Company

Figure 316 White Lead Paint in Paste Form

sulfides of copper, lead, iron, and other metals. The matte is treated again in the blast furnace to recover the lead, silver, and gold which it contains.

15. Refining

Lead bullion is hard because it contains alloys of lead with other metals. The more easily oxidized metals are separated by melting the bullion in a reverberatory furnace in the presence of air. Arsenic, zinc, antimony, copper, and some of the lead are changed to oxides, which float on the melted lead and are removed by skimming. The lead is then drawn off and further purified by one of the following methods.

(1) *Parke's Process* The lead is melted with a small amount of zinc, which does not mix with

the lead. The zinc layer dissolves silver, gold, and copper and floats on the heavier layer of lead. When the top layer cools, it forms a crust, which is easily skimmed off. The lead must be treated with zinc three or four times to remove the other metals. The small amount of zinc that is not removed by skimming is separated from the lead by changing it into the oxide. This is accomplished by blowing air and steam into the melted mass.

(2) *The Belts Process* This is an electrolytic process of refining. Anodes made of the lead bullion are suspended in a bath of fluosilicic acid and lead fluosilicate, $PbSiF_6$. The lead dissolves from the anodes and is deposited on cathodes made of sheets of pure lead. The process is very much like the electrolytic refining of copper. The anode mud contains silver, gold, and bismuth. The more active metals, such as iron and zinc, dissolve but remain in the solution.

16. Physical Properties

Lead is a soft, malleable metal. A freshly cut surface is brightly lustrous, but this is soon covered in the air with a coat of dull gray material containing the basic carbonate, lead monoxide, and particles of lead. The metal has a very low tensile strength, a greater density (11.3 g per cc) than any other common metal; and a melting point of 327.5° . When heated to a temperature slightly below its melting point it becomes softer and more plastic. In this condition it can be made into lead pipes, wire, and rods. It is only a moderately good conductor of electricity.

17. Uses

Lead has a few properties that make it suitable for a number of uses. It is soft and easily melted, hence it is easily molded and worked. It is not very active chemically, and therefore does not corrode easily and is durable under conditions that cause many of the more active metals to wear away quickly. The use of lead in making the chambers of a sulfuric acid plant has already been mentioned (page 501). It is also used to make pipes and troughs for the conveyance of liquid wastes, traps for sinks, and so on. It is sometimes used as a lining in pipes, tanks, sinks, and other apparatus and containers whose outside walls are made of less resistant metals. It is utilized as a covering or sheath for telephone and other electrical cables, to make the plates of storage batteries, in the manufacture of white lead and other compounds of lead; and in the production of many alloys, some of which are pewter, shot, solder, type metal, and fuse metal.

18. Chemical Properties

Lead is directly above hydrogen in the electromotive series. This means that it is a slightly active metal. Its activity in reactions with most reagents is further decreased, because the compounds formed in these reactions are insoluble and act as protective

coverings for the metal. A freshly cut surface tarnishes rapidly in the air because of the formation of a thin coat of the oxide and basic carbonate. It does not react noticeably with cold water and only very slightly with hot water. When lead pipes are used for the conveyance of hard water, the pipes become coated with a layer of lead carbonate and lead sulfate. If soft water which contains dissolved oxygen flows through the pipe, lead hydroxide, $\text{Pb}(\text{OH})_2$, is formed. The hydroxide is somewhat soluble in water and, like all lead compounds, is poisonous, for this reason, lead pipes are not suitable for the conveyance of drinking water. Hydrochloric acid attacks lead only slightly, and dilute sulfuric acid has still less effect. The action of both acids is retarded by the formation of insoluble compounds. Sulfuric acid solutions containing more than 77 per cent of H_2SO_4 act upon lead more rapidly than the dilute acid, since lead sulfate is more soluble in concentrated sulfuric acid and therefore does not protect the metal. Nitric acid dissolves lead, forming lead nitrate and liberating nitric oxide or nitrogen dioxide (cf. copper, page 484). Many of the weak acids, such as hydrosulfuric, carbonic, and acetic, act upon the metal.

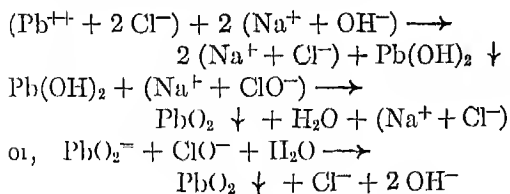
The most familiar compounds of lead are those in which the metal is bivalent. The hydroxide, $\text{Pb}(\text{OH})_2$, is amphoteric, but it is more basic than acid, and hence lead is more likely to be found as Pb^{++} than as PbO_2^{-} ion. The bivalent salts of lead, if soluble, are moderately hydrolyzed in solution. Basic salts are often produced as a result of hydrolysis. Lead also forms a series of compounds in which it acts as a quadrivalent element. Among these are lead dioxide, PbO_2 , and salts corresponding to $\text{Pb}(\text{OH})_4$, or H_2PbO_4 , which act as an acid. All soluble lead compounds are poisonous. They act as accumulative poisons, since their elimination, through the kidneys, is very slow. Great care is exercised to prevent lead poisoning in the industries which involve the use of lead or its compounds. Poisoning

may result from the entrance of lead into the body through the mouth or nostrils as dust in the air that is breathed

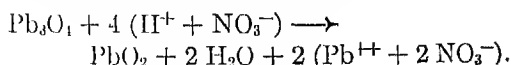
19 Oxides and Hydroxides of Lead

Lead monoxide, PbO , occurs in two crystalline forms, one red and one yellow in color. The latter is called *massicot*. The commercial form called *litharge* is buff, because it contains some red lead. It may be produced by heating lead in the air, but the commercial product is made, largely, during the refining of lead and silver. It is used in making lead glass, in manufacturing rubber goods, storage batteries, glazes for pottery, and paints. It is used as a "drier" for linseed oil in paints, where it probably acts as a catalyst for the reaction in which linseed oil absorbs oxygen from the air and is oxidized to a hard film. A mixture of litharge and glycerine is used by plumbers as a rapidly hardening cement.

Lead dioxide, PbO_2 , may be produced as a deposit on the anode when acid solutions of lead salts are electrolyzed. (Review the section on the Storage Battery, page 638.) It may also be produced by the action of vigorous oxidizing agents — such as chlorine, sodium hypochlorite, bleaching powder, or calcium hypochlorite — upon lead hydroxide or sodium plumbite, Na_2PbO_2 .



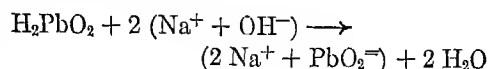
Lead dioxide is also produced by the action of nitric acid upon red lead, Pb_3O_4 .



It is a brown powder. It is a very good oxidizing agent, and most of its uses depend upon this property. It is used in storage batteries, in making the "striking" surface on boxes of safety matches, and in many

reactions involving oxidation, such as the preparation of potassium permanganate from manganese dioxide, or the liberation of chlorine from hydrochloric acid.

Lead monoxide and the corresponding hydroxide, $\text{Pb}(\text{OH})_2$, which is precipitated when an alkali is added to a solution of a lead salt, are soluble in acids and in bases. *Plumbous* salts, such as PbCl_2 , are formed with acids, and *plumbites* are formed in solutions of bases.



As compared with stannous hydroxide, $\text{Pb}(\text{OH})_2$ is a slightly stronger base.

Lead dioxide dissolves slightly in concentrated solutions of alkalies, forming *plumbates*, as Na_2PbO_3 , or $\text{Na}_2\text{Pb}(\text{OH})_6$. Toward acids, the dioxide is almost inert as regards basic properties. It reacts slowly with nitric acid, but lead is reduced to the divalent state, and oxygen is liberated in the reaction. Under ordinary conditions, it oxidizes hydrochloric acid to liberate chlorine, but a liquid lead tetrachloride may be formed at very low temperatures. In glacial acetic acid the dioxide dissolves to form lead tetra-acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$, which is completely hydrolyzed by water.

20 Red Lead, Pb_3O_4

Red lead, or *minium*, is not an oxide but a compound of two lead oxides, PbO and PbO_2 . This compound, Pb_2PbO_4 , may be called *plumbous plumbate* ($2 \text{PbO} \cdot \text{PbO}_2$). It is a red powder and is produced by heating the monoxide in the air at temperatures between 450° and 500° . It is used in glass-making and as a paint pigment, especially in paint applied as the first coat for structural iron and steel. This paint is very effective in protecting the metal against corrosion. Mixed with linseed oil, it makes a good seal for joints in pipe lines.

The so-called lead trioxide, Pb_3O_3 , is also a salt, PbPbO_3 . This compound is the metaplumbate, while red lead is the orthoplumbate. The former corresponds to metaplumbic acid, HPbO_3 , and the latter to orthoplumbic acid, $\text{H}_4\text{PbO}_4(\text{Pb}(\text{OH})_4)$.

21. Lead Nitrate, $\text{Pb}(\text{NO}_3)_2$

This is the salt of lead which is commonly employed in the laboratory to prepare solutions of the plumbous ion, Pb^{++} . It is prepared by the action of nitric acid upon lead or lead monoxide. It is used as a mordant, in matches, and in the preparation of other lead compounds. When the crystals of the salt are heated, lead monoxide is produced by decomposition. It is soluble in water, but hydrolysis produces a slightly soluble basic nitrate, except in the presence of an excess of acid.

22. Lead Acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$

Lead monoxide dissolves in acetic acid to form plumbous acetate, which crystallizes as the hydrate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$. This salt of lead has a sweet taste and is called *sugar of lead*. It is used in preparing ointments for the treatment of certain skin diseases and in the dyeing and printing of cloth. It is very poisonous.

23. Lead Halides

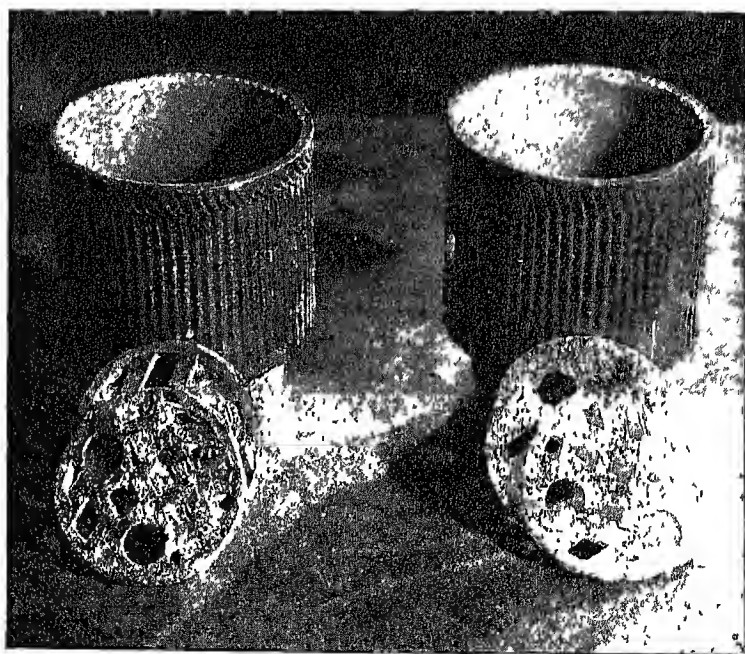
The halides of lead, of which lead chloride is the most familiar, are prepared by the action of the hydro-halogen acids upon lead monoxide or by precipitation reactions between plumbous ion

and the halide ions. They are slightly soluble in cold water and somewhat more soluble in hot water. When their hot saturated solutions are cooled, the chloride and bromide separate as gleaming white crystals, and the iodide forms bright golden-yellow spangles.

In the detection of lead in a solution which contains other metals, lead chloride is precipitated along with the chlorides of silver and mercury (-ous) by the addition of a soluble chloride. The lead chloride of the residue, which is separated by filtration from the solution containing other metals, is then removed by dissolving it in hot water, in which silver and mercurous chlorides do not dissolve appreciably. The lead ion may then be detected in the solution obtained by washing the residue with hot water by adding sodium or potassium chromate, which precipitates the lead as lead chromate, PbCrO_4 .

24. Paints, White Lead

This substance is the basic carbonate of lead, $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$. It is best known as a substance used to provide the *body* of paints. Paints are made by grinding an insoluble, heavy, durable substance in linseed oil, hemp oil, or tung oil. The body must



Courtesy of National Lead Company

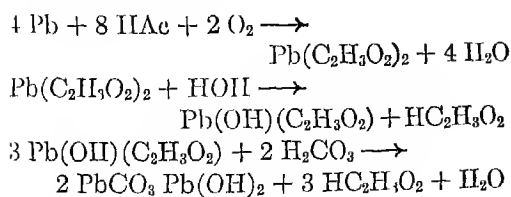
Figure 317 Pots and Lead Buckles Used in Making White Lead
Buckles before and after corrosion are shown.

possess good "hiding" power in covering the surface to which the paint is applied. White lead is one of the most widely used substances for this purpose, but lithopone and titanium dioxide are also used. Coloring materials are added to form paints of the desired color or shade, these are called *pigments*.

Many paints also contain certain fillers, such as calcium or barium sulfate, kaolin, or calcium carbonate. These substances, if used in excess, lower the durability of paints, but when added in carefully calculated proportions lower the cost and at the same time make the paint spread more easily.

The oil used in paints must dry, or harden, when exposed to the air, to form a durable, flexible coating on the painted surface. The drying process involves oxidation, which is accelerated by heating the oil with *driers*, such as the oxides of lead and manganese.

White lead is usually made by the *Carter* or by the *Old Dutch* process. The latter has been used for several centuries. In this process the lead is cast in the form of thin, perforated disks, called "buckles." These disks are stacked in earthenware vessels containing a shallow layer of dilute acetic acid. The vessels are stacked in tiers in a large room and covered with spent tanbark, which ferments, liberating carbon dioxide and producing heat, which vaporizes the acetic acid. White lead is produced by the action of acetic acid vapor, carbon dioxide, water, and oxygen upon the lead. The process requires three or four months for completion. We may think of the following equations as representing the changes which occur, although the exact nature of the reactions is unknown.



The Carter process produces white lead more rapidly than the Old Dutch process.

Melted lead is atomized by a blast of compressed air. This finely divided material is then placed in revolving wooden drums, which also contain acetic acid and carbon dioxide. The reactions are completed in about two weeks. White lead is also manufactured by an electrolytic process. The cell consists of two parts, separated by a porous diaphragm; one part contains a solution of sodium carbonate and an iron cathode; the other contains sodium acetate, acetic acid, and a lead anode. Lead ions are set free at the anode, by the action of acetic acid upon the metal, and move toward the cathode, near this electrode, they react with hydroxyl and carbonate ions to form basic lead carbonate or white lead.

The United States produces about 200,000 tons of white lead annually.

25. Other Compounds of Lead

Lead chromate, PbCrO_4 , is used as a yellow paint pigment, which is called *chrome yellow*. *Lead sulfate*, PbSO_4 , is an insoluble salt of lead. It is produced by adding a soluble sulfate to a solution of a lead salt. Precipitated lead sulfate is used to some extent as a paint pigment. *Sublimed white lead* is a mixture of lead sulfate and lead monoxide. It is produced by heating galena and is used as a pigment. *Lead arsenate*, $\text{Pb}_3(\text{AsO}_4)_2$, is a white, slightly soluble salt. It is prepared by mixing solutions of lead acetate and sodium arsenate, and is used as an insecticide. *Lead sulfide*, PbS , is one of the very slightly soluble sulfides, it is precipitated by hydrogen sulfide from solutions containing the lead ion in the presence of moderate concentrations of hydrochloric acid. In qualitative analysis it is precipitated, therefore, in the group that contains copper and mercury. *Lead tetraethyl*, $\text{Pb}(\text{C}_2\text{H}_5)_4$, is used in making "ethyl" gasoline. It is made by treating an alloy of sodium and lead with ethyl bromide.

OTHER ELEMENTS OF GROUP FOUR

26. Germanium

This element is a grayish-white, brittle, durable, metallic substance. It melts at 958° and has a density of 5.36 g. per cc. It

occurs in small amounts in the sulfide ores of several of the metals, but it is usually produced as a by-product of the refining of zinc. Like tin and lead, it forms two oxides, GeO and GeO_2 , both of these are amphoteric. The metal is produced by reducing the oxide with carbon. In many of its compounds germanium resembles carbon and silicon; but it differs from these elements in forming some compounds in which a more definitely metallic character is revealed. Thus, its tetrachloride, GeCl_4 , is volatile like CCl_4 , and it also forms a compound GeHCl_3 , which is analogous to chloroform. Sodium germanate, Na_2GeO_3 , is analogous to sodium carbonate or sodium silicate. On the other hand, GeO dissolves in acids to form divalent germanium compounds of a salt-like character. In this respect the element is unlike carbon.

27 Thorium

This element is the only member of the A division of group four that is strictly metallic. It occurs in the mineral *thorite*, ThSiO_4 , and in monazite sand (page 706). The latter is the commercial source of the compounds of thorium. The sand contains amounts of thorium oxide that vary from 1 up to 15 or 20 per cent. This oxide is extracted for the preparation of Welsbach gas mantles (page 574). The metal can be prepared by the reduction of the oxide with an alloy of the rare-earth metals called misch metal (page 706). It is heavy and melts at 1850° . In many respects it resembles platinum. In its compounds thorium acts as a metal and displays a valence of 4 (positive). The hydroxide, $\text{Th}(\text{OH})_4$, dissolves in acids to form salts, such as ThCl_4 , $\text{Th}(\text{NO}_3)_4$, and $\text{Th}_3(\text{PO}_4)_4$. It also forms basic salts such as ThOCO_3 , double salts such as $\text{KNO}_3 \cdot \text{Th}(\text{NO}_3)_4 \cdot 9 \text{H}_2\text{O}$, and complexes, of which K_2ThF_6 is an example. The radioactivity of thorium has been mentioned in connection with the general treatment of radioactivity in Chapter 17.

Review Exercises

- 1 Describe the methods used in the production of tin from cassiterite.
- 2 How is tin recovered from tin plate scrap or waste, such as tin cans?
- 3 How does stannic chloride differ from ordinary salts, such as sodium chloride?
- 4 Why does stannic sulfide dissolve in a solution of ammonium sulfide? Why does stannous sulfide dissolve in ammonium polysulfide but not in ammonium sulfide?
- 5 Write equations to show the reactions which occur when tin is treated with a boiling solution of (a) HNO_3 and (b) NaOH .
- 6 How can stannous chloride be prepared from (a) tin and (b) stannic chloride?
- 7 In what way is tin less effective than zinc in protecting the surface of iron?
- 8 Explain the meaning of the term *tin disease*.
- 9 Suggest chemical reactions which could be used to distinguish between tin and lead.
- 10 What is one objection to the use of white lead in paints?
- 11 Outline the essential steps in the production of lead from galena.
- 12 Identify lead bullion, chrome yellow, red lead, sugar of lead, and white lead.
- 13 Describe the Old Dutch process for the manufacture of white lead.
- 14 Make a list of representative compounds of lead and tin.
- 15 Enumerate the uses of tin, lead, thorium, and titanium and their compounds.
- 16 Why does dilute sulfuric acid have little effect upon lead?
- 17 A sample of pure white lead evolved 100 ml (standard) of carbon dioxide when it was treated with an acid. What was the weight of the sample?
- 18 A solution containing mercuric chloride was treated with sufficient stannous chloride to completely reduce the mercuric ion to metallic mercury. If the mercury resulting from the reaction weighed 1.4 g and the volume of the solution was 400 ml, what was the concentration of the mercuric chloride in the solution?
- 19 The iron in a sample of iron ore weighing 10 g was completely converted into ferric chloride,

FeCl_3 , which then was reduced to FeCl_2 by SnCl_2 . If 1.5 g of SnCl_2 was used, what was the percentage of iron in the ore?

20. What weight of PbSO_4 can be produced by the oxidation of 100 g of PbS ?

21. A sample of PbO weighing 100 g is first converted into red lead and then into PbO_2 with the help of nitric acid. What weight of PbO_2 can be produced?

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THE METALS OF GROUPS FIVE, SIX, AND SEVEN

1 Introduction

The elements of Division A of the fifth group of the periodic classification are metals. These are vanadium, columbium, and tantalum. Arsenic and antimony, which have certain metallic characteristics, and bismuth, which is a metal, have been discussed in another chapter (page 519). Group six contains chromium, molybdenum, tungsten, and uranium as its representatives among the metals, all of these are in Division A of this group. The A Division of group seven contains manganese, manganum, and rhenium. Manganese is the only one of these metals that is well known. The two others have only recently been discovered and very little definite information is known about them at this time.

VANADIUM

This element was discovered in 1830. It occurs as *vanadinite*, $3\text{Pb}_3(\text{VO}_4)_2\text{PbCl}_2$; *carnotite*, $2\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, *roscoelite*, a vanadium bearing mica, *patronite*, a complex sulfide, and *pucherite*, BiVO_4 . The principal producing localities are in Peru, Africa, Mexico, and in Arizona, Colorado, and Utah.

The metal is difficult to prepare because of its tendency to combine with carbon, nitrogen, and other elements. It can be prepared by reducing the oxide with misch metal, or by reducing VCl_3 with hydrogen. Commercially, the alloy with iron, which is called *ferrovanadium*, is produced instead of

the pure metal. This alloy is used in the steel industry to produce vanadium steel. It is made by reducing the oxides of iron and vanadium with carbon. Vanadium steel has a high tensile strength and great resistance to shock and vibration. It is used in high-speed tools, in many automobile parts, as car wheels, and in locomotives.

2 Properties and Compounds

Metallic vanadium is silver-white in color, hard, brittle, and crystalline. It is converted into the oxides, VO_2 and V_2O_5 , when it is heated in air or in oxygen, and with chlorine and bromine it forms VCl_3 and VBr_3 . It reacts, at high temperatures, with carbon to form the carbide, VC , with nitrogen to form the nitride, VN , and with sulfur to form the sulfides, VS_2 and V_2S_5 . It dissolves in concentrated acids to form vanadous or vanadic salts and in alkalis to form vanadates, such as NaVO_3 or Na_3VO_4 . The metal forms four oxides: VO , V_2O_3 , VO_2 , and V_2O_5 . The monoxide is basic, forming salts, such as *vanadous sulfate*, VSO_4 , or *vanadium dichloride*, VCl_2 . These salts are violet in color. The trioxide, V_2O_3 , or the corresponding hydroxide, dissolves in acids to form solutions of vanadic salts, of which VCl_3 is an example. These salts are green. The dioxide, VO_2 , dissolves in solutions of sodium, potassium, or ammonium hydroxide to form *vanadates*, which are black salts of vanadous acid, $\text{H}_2\text{V}_3\text{O}_8$ ($4\text{H}_4\text{VO}_4 - 7\text{H}_2\text{O} \rightarrow \text{H}_2\text{V}_3\text{O}_8$). It also dissolves in acids, forming blue *vanadyl* salts, of which VOCl_2 and VOSO_4 are typical. The pentoxide, V_2O_5 , forms salts of three vanadic acids: NaVO_3 , *sodium metavanadate*, $\text{Na}_4\text{V}_2\text{O}_7$, *sodium pyrovanadate*, and Na_3VO_4 , *sodium orthovanadate*. Pervanadyl salts are also known. Pervanadyl fluoride, for example, is VOF_3 and the corresponding sulfate is

$(VO)_2(SO_4)_3$ These are prepared when concentrated acids act upon the pentoxide. With hydrochloric acid, the pentoxide acts as an oxidizing agent, liberating chlorine. Orthovanadic acid and the vanadates are yellow in color. The pervanadyl salts are usually red or reddish-brown substances.

COLUMBIUM

This element (sometimes called niobium) is found in small deposits in many localities. The principal mineral is *columbite*, which contains $Fe(CbO_3)_2$. It also occurs in other minerals which contain tantalum, titanium, and the rare-earths. The metal is used in making stainless steel and in a few alloys which are used in making jewelry. Ferrocolumbium, made by reducing columbite with carbon, is used to make stainless steel. The element forms four oxides which correspond to the four oxides of vanadium. Its best known compounds are the columbates, which are salts of *ortho*, *meta*, or *pyro columbic acid*, salts of *fluocolumbic acid*, H_2CbF_7 , chlorides, $CbCl_5$ and $CbCl_3$, and oxy-salts, such as $CbOCl_3$. These are closely related in properties to the corresponding compounds of vanadium. The metal is prepared by the electrolysis of the fused double fluoride of columbium and potassium, K_2CbF_7 .

TANTALUM

This metal occurs in *tantalite*, which is essentially $Fe(TaO_3)_2$, and in minerals that also contain columbium. The metal, which is prepared by the electrolysis of fused potassium tantalum fluoride, K_2TaF_7 , or reduction methods in the same manner as vanadium, is hard but ductile, has a density of 16.6, and melts at about 1800° . It is extremely resistant to all reagents, except strong alkalis and hydrofluoric acid, at ordinary temperatures. Before being displaced by tungsten, which is more easily prepared and has a higher melting point, it was used to make the filaments of electric lamps. It readily adsorbs gases, and for this reason is used to remove traces of gases in radio tubes. It is also used in making electrodes for current rectifiers, in the manu-

facture of surgical instruments, as electrodes in radio tubes, and as a substitute for platinum in making articles and utensils which are used in the laboratory.

At a red heat the metal burns in the air to form the pentoxide, Ta_2O_5 . This oxide reacts when fused with alkali hydroxides to form *tantalates*, of which $Na_5Ta_6O_{19}$ is an example. Metatantalates, such as $NaTaO_3$, are also known and the corresponding acid, $HTaO_3$, is an insoluble, fairly stable compound. The metal reacts with fluorine, chlorine, and bromine to form penta-halides, $TaCl_5$, TaF_5 , and $TaBr_5$. These are hydrolyzed completely by water, forming a precipitate of $HTaO_3$. Salts of *fluotantalic acid*, H_2TaF_7 , are also known.

CHROMIUM

3. Occurrence

This element is the most abundant metal of group six. Its most important ore is *chromite*, $Fe(CrO_2)_2$. It also occurs in small amounts with aluminum in igneous rocks, as the mineral *crocoite*, $PbCrO_4$, and in some precious stones (page 702). About one half of the world's supply of chromite comes from Rhodesia. Russia, New Caledonia, India, Cuba, Greece, and Turkey produce smaller amounts. The mineral occurs in the United States in Montana, Tennessee, Arkansas, Georgia, Oregon, and California. Until about 1875, Maryland and Pennsylvania supplied most of the world's supply of chromite, but at the present time much of the ore used in the United States is imported. Our normal yearly requirement is 250,000 to 300,000 tons.

4 Metallurgy

To prepare compounds of chromium, chromite ore is fused with sodium carbonate in the presence of air. The iron is oxidized to Fe_2O_3 and the chromium is converted into sodium chromate, which is dissolved in water and recovered by evaporation. Other compounds of the element may be prepared from this product. When chromite is reduced by

carbon in an electric furnace, an alloy of chromium and iron, called *ferrochrome*, is produced. This is used in making chromium steels. The pure metal can be prepared by reducing the oxide, Cr_2O_3 , with aluminum by the Goldschmidt process. The metal may also be deposited electrolytically on iron or copper cathodes from a solution containing chromic acid and sulfate, phosphate, or borate ions. During recent years chromium plating for radiators and other parts of automobiles, plates for engraving, bathroom fixtures, tableware, and other articles has become more popular than nickel plating. To secure dense deposits of chromium, the article is first plated with copper, then with nickel, and finally with chromium.

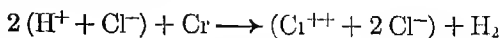
5 Physical Properties and Uses

Chromium is a very hard, crystalline, silvery-white metal. It melts at 1615° . It is used to electroplate many articles made of other metals because of its resistance to corrosion, its hardness, and its lasting bright luster, which resembles the color of platinum. It is also used to make several alloys. The most important of these are the chromium steels, which are made by adding ferrochromium to melted steels. These steels contain from 1 up to 20 per cent of chromium. They are hard, strong, and tough, and resistant to corrosion and tarnishing. Such steels are used to make bearings, valves, cutlery, armor plate, shells, safes, bank vaults, and high-speed tools. Stainless steel, which is used in making cutlery, contains 12 to 14 per cent of chromium. Stainless iron contains 16 per cent or more of chromium; it is used in nitric acid plants because of its great resistance to corrosion by that acid. Alloys of iron with chromium and nickel are used in apparatus that must withstand corrosive action in the chemical manufacturing industries. Almost all alloy steels contain some chromium in addition to nickel, vanadium, tungsten, or other metals. *Nichrome* (nickel, chromium, and iron) and *chromel* (nickel and chromium) are used in the form

of wire as electrical resistance in making the heating units of small electrical furnaces and small heaters. *Stellite*, which is used in making cutting tools, contains chromium, tungsten, and cobalt. *Illium* is an alloy made of chromium, nickel, iron, copper, aluminum, molybdenum, silicon, and manganese. It is sometimes used as a substitute for platinum.

6 Chemical Properties

Chromium does not tarnish in the air at ordinary temperatures, but it burns, when heated to a high temperature, producing the oxide, Cr_2O_3 . When heated to redness it liberates hydrogen from steam. When placed in acids the behavior of the metal varies, depending upon its previous treatment or method of production. Like iron and many other metals it has an *active* and a *passive* state. Nothing of a definite nature is known concerning the difference between these two states. Chromium produced by the Goldschmidt process, or after it has been dipped in concentrated nitric acid or chromic acid, or exposed to the air for some time, is passive. In this state, the metal does not react with nitric, hydrochloric, or sulfuric acid, and does not displace other metals that lie below it in the electrochemical series from solutions of their salts. The passive state is not permanent. It may be changed to the normal, active condition by standing in solutions of the acids, by heat, or even by a shock or jar. The passive state may be due to a film of oxide on the surface of the metal, to different allotropic modifications, or to the production of a strain of some kind that renders the atoms on the surface inactive. The active metal dissolves in the non-oxidizing acids to produce chromous salts and to liberate hydrogen.



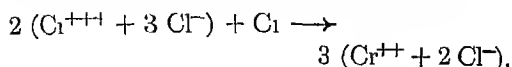
Chromium lies between zinc and cadmium in the electrochemical series.

The valence number of chromium in its compounds is 2, 3, or 6. In its divalent state,

the element is basic, in the trivalent state amphoteric, and in the hexavalent state acidic. The oxides, hydroxides, acids, and typical salts are shown in Table 43.

7. Chromous Compounds, Cr^{++}

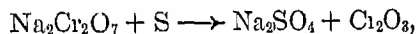
Chromous hydroxide, $\text{Cr}(\text{OH})_2$, is basic. It is readily oxidized in the air. Solutions of the chromous salts are prepared by dissolving the metal in acids or by reducing solutions of chromic salts with chromium or zinc.



Chromous compounds resemble those of divalent iron. They are very active reducing agents and are oxidized readily in the air. Because of this difficulty in preserving them in the pure state, they are of little practical importance.

8. Chromic Compounds, Cr^{+++} and CrO_2^-

The oxide, Cr_2O_3 , and the corresponding hydroxide, $\text{Cr}(\text{OH})_3$, are amphoteric. The hydroxide is produced by adding an alkali hydroxide to a solution of a chromic salt, such as CrCl_3 . The oxide is formed when the metal is heated in the air, when a dichromate is heated with sulfur,



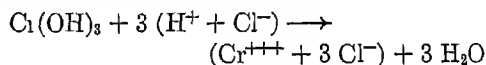
or, simply, by heating ammonium dichromate



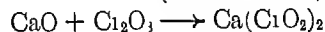
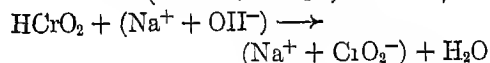
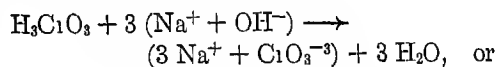
It is the most stable of the three oxides. It has a green color and is used as the pigment called *chrome green*. It is also used to color glass and ceramics, to which it imparts a green or blue color. It also has some use as a catalyst.

When the hydroxide is prepared by precipitation it is a light blue gelatinous substance which resembles aluminum hydroxide (page 701). The precipitate is really a hydrous oxide and is sometimes assigned the formula, $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$. In writing equations to show its reactions with acids and bases we shall follow, however, the usual practice of considering the compound as the normal hydroxide, $\text{Cr}(\text{OH})_3$.

Chromic hydroxide dissolves in acids to form solutions of chromic salts



It also dissolves in alkali hydroxides to form chromites, and similar compounds are formed when Cr_2O_3 is fused with the oxides of metals



The hydroxide is precipitated again when solutions of the alkali hydroxide in which it has dissolved are boiled. The reprecipitated

TABLE 43

The Compounds of Chromium

Oxide	Hydroxide	Properties of hydroxide	Salts	Color of the ions
CrO	$\text{Cr}(\text{OH})_2$	basic	CrCl_2 , chromous chloride	blue
Cr_2O_3	$\text{Cr}(\text{OH})_3$	basic	CrCl_3 , chromic chloride	green-violet
	or H_3CrO_3 or HCrO_2	acidic	NaCrO_2 , sodium chromite	green-black
CrO_3	H_2CrO_4	acidic	Na_2CrO_4 , sodium chromate	yellow
	or $\text{H}_2\text{Cr}_2\text{O}_7$	acidic	$\text{Na}_2\text{Cr}_2\text{O}_7$, sodium dichromate	red

compound is pale green in color and is a less completely hydrated oxide than the original precipitate

Chromite, the principal ore of chromium, is ferrous chromite, $\text{Fe}(\text{CrO}_2)_2$. Other chromites exist naturally

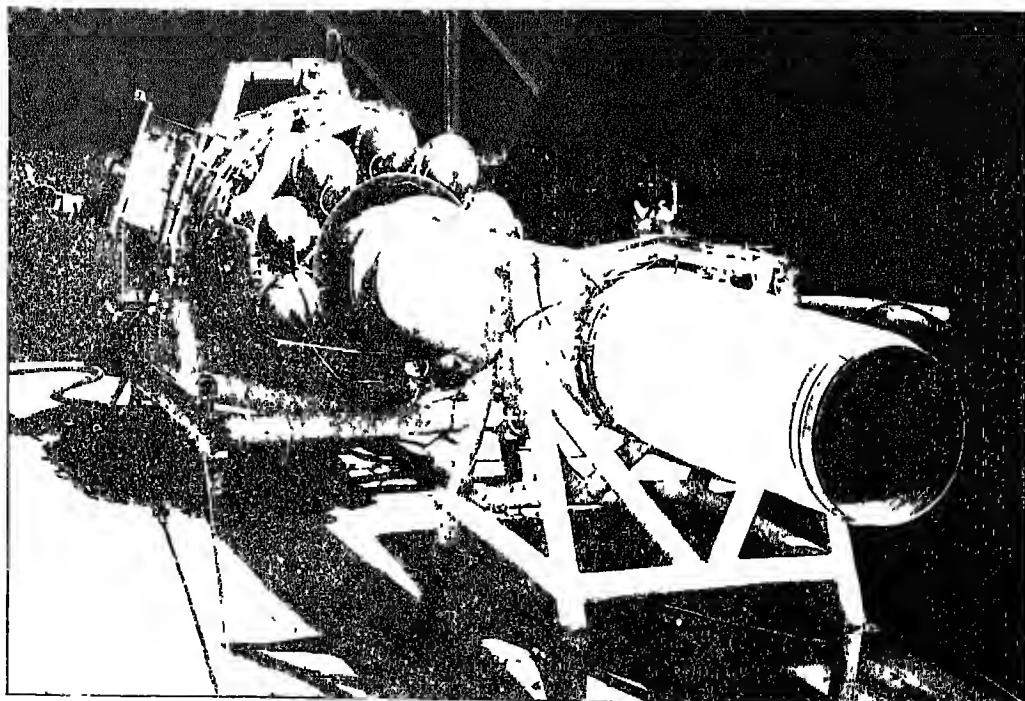
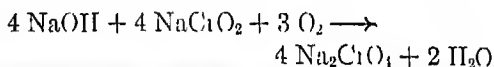
Chromic chloride, CrCl_3 , and chromic sulfate, $\text{Cr}_2(\text{SO}_4)_3$, are the best known salts of trivalent chromium. Solutions of the chloride are either violet or green in color. When the chloride is dissolved in water to form dilute solutions, the chromic ion appears to combine with six molecules of water to form the violet colored ion, $\text{Cr}(\text{H}_2\text{O})_6^{+++}$, and the solution contains the corresponding chloride $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$. All of the chloride ion may be precipitated from this solution by the addition of silver nitrate. In more concentrated solutions, and after standing for some time, this compound is transformed into $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$, which is green. The complete compound in this solution is $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+\text{Cl}^-$. This formula is indicated by the fact that silver nitrate precipitates only one third of the chlorine atoms in the solution as silver chloride. This

behavior indicates that two of the chlorine atoms of the compound are not present in the solution as chloride ions but are attached to the chromium atom as portions of a complex, slightly ionized ion. Chromium also forms similar complex ions with ammonia and with several radicals, such as CNS^- and CN^- .

Chromic sulfate, too, exists in violet and green modifications. When it is dissolved in a solution that also contains potassium sulfate, red or ruby crystals of potassium chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, form upon evaporation of the water. This substance is used in tanning leather.

9. Chromic Acid and the Chromates

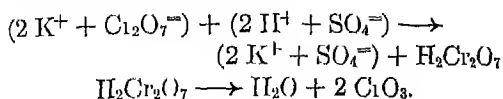
Salts of chromic acid, H_2CrO_4 , are produced by heating a chromite, chromic oxide, or chromic salts, with an alkali hydroxide or carbonate in the presence of air. The oxidation of sodium chromite is shown by the following equation:



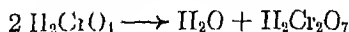
Courtesy of The International Nickel Company, Inc.

Figure 318 Stainless Steel Containing Chromium and Nickel is Used in Jet Engines
The alloy is used in the combustion chambers, tail pipe, and wrappings of this Navy fighter plane engine

The trioxide, CrO_3 , is produced as scarlet needle-like crystals, when sulfuric acid is added to a concentrated solution of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$

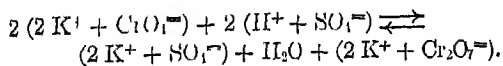


Free chromic acid cannot be prepared. It loses water forming dichromic acid



The dichromic acid, in turn, loses water and forms the anhydride as shown above

When dilute sulfuric acid, or another acid, is added to a yellow solution of potassium chromate, the color changes to red or orange, and upon evaporation, crystals of potassium dichromate separate



The dichromate is converted again into the chromate when it is treated with potassium hydroxide. This behavior indicates that in solution the chromate ion, $\text{CrO}_4^{=}$, and the dichromate ion, $\text{Cr}_2\text{O}_7^{=}$, are in equilibrium, and that this equilibrium may be shifted in one direction by the addition of hydroxyl ion and in the other direction by the addition of hydrogen ion. The equilibrium is also indicated by the precipitation of BaCrO_4 , when barium chloride is added to a solution containing potassium dichromate, provided that the hydrogen ion concentration of the solution is not very great.

A mixture of sodium dichromate and sulfuric acid is used as a cleaning solution for glass and porcelain ware in the laboratory. The dichromates are used as oxidizing agents in many reactions. They are also used in tanning leather; the dichromate is first reduced to a compound of trivalent chromium, and the chromic hydroxide which is formed by hydrolysis reacts with the nitrogenous substances in hides to make a permanent leather that does not decay. Dichromates are also used in photography. Lead chromate, PbCrO_4 , and barium chromate, BaCrO_4 , are used as yellow pigments.

When heated with sodium chloride and concentrated sulfuric acid, a dichromate forms a volatile, dark red liquid called *chromyl chloride*, CrO_2Cl_2 . This reaction is used to detect chlorine. The addition of hydrogen peroxide to an acid solution of a chromate forms a blue substance, which may be extracted with ether; the composition of this compound is not definitely known, but it may be HCrO_5 , a perchromic acid. This reaction is a reliable and delicate test for the chromate ion.

MOLYBDENUM

In 1778, Scheele produced the oxide of a new element from a mineral, now called *molybdenite* and composed essentially of MoS_2 . This is still the principal mineral source of the element. Molybdenum also occurs in the form of molybdates, of which lead molybdate, PbMoO_4 , is most important. This is the mineral called *wulfenite*. Most of the molybdenum produced comes from Norway or from Colorado and New Mexico.

10. Preparation of the Metal, Physical Properties, and Uses

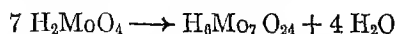
Molybdenite ores are roasted and then treated with ammonium hydroxide which dissolves the oxide of molybdenum, forming ammonium molybdate. This substance is recovered by evaporation, and the solid salt is ignited in order to drive off the ammonia. The final product is molybdenum trioxide, MoO_3 . This oxide is then reduced with carbon or hydrogen in the electric furnace. This process gives the metal in the form of a finely divided powder. Ferromolybdenum is produced in the same way as ferriochromium; it is used to make alloy steels. These steels are resistant to chemical action, hard, strong, and tough. They usually contain some chromium and other metals and are used for the same purposes as those described for chrome steels (page 722). Pure molybdenum has a silvery-white color. The powdered

metal produced by the reduction of the oxide can be made into wire by first pressing the powder into a rod and passing an electrical current through it. The resistance of the rod produces enough heat to partially fuse the particles of the metal and cement them together. This material may then be rolled into sheets or drawn into wire. The metal melts at about 2625°.

In addition to its use in the manufacture of steels, molybdenum is used to make the supports for the filaments in electric lamps; to make certain portions of the interior structures of radio tubes, to make the terminals, or points, of spark plugs and automobile distributors; and as electrical resistance in small electrical furnaces.

11. Chemical Properties and Compounds

The metal reacts with oxygen, carbon, fluorine, chlorine, bromine, and sulfur but usually only at elevated temperatures. It does not dissolve in non-oxidizing acids or in solutions of the alkali hydroxides. It is converted by nitric acid into the trioxide MoO_3 . In its compounds, the element has positive valences of 2, 3, 4, 5, and 6. In the laboratory the most familiar compound of molybdenum is ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$, which separates as crystals when the trioxide, MoO_3 , is dissolved in ammonium hydroxide and the solution is evaporated. This compound is a salt of one of the condensed molybdic acids. The normal form of molybdic acid is H_2MoO_4 , which forms yellow crystals that separate from a solution of the oxide in water. The condensed acid referred to above may be explained by the following equation



The fusion of the trioxide with carbonates or oxides of the metals results in the formation of molybdates such as Na_2MoO_4 . Ammonium molybdate is used in the detection and quantitative determination of phosphate ion. When a solution containing a phosphate is made strongly acid with nitric acid and a

solution of ammonium molybdate is added, a yellow, powdery precipitate is produced when the mixture is heated. The yellow compound is called *ammonium phosphomolybdate* and has the approximate formula $(\text{NH}_4)_3\text{PO}_4 \cdot 12 \text{MoO}_3$, but the composition may vary slightly as to the amount of MoO_3 that the compound contains.

In its lower valence states molybdenum is basic and in its higher valence state it is acidic. Many of the compounds of the metal are deeply tinted and are used as coloring for cloth and leather and in making the painted designs and glazes of chinaware. One such compound, which is called molybdenum blue, is made by the reduction of molybdic acid. It is probably a molybdate of quadrivalent molybdenum, $(\text{MoO})_2(\text{MoO})_2$, in which the MoO^{+4} group acts as the molybdenyl radical and corresponds to the hydroxide, $\text{MoO}(\text{OH})_2$. The chlorides, MoCl_2 , MoCl_3 , MoCl_4 , and MoCl_5 are all known, but some of these compounds are not stable. The simple ions are readily changed into complex ions of many kinds, of which $\text{MoCl}_5^{=}$, $\text{Mo}(\text{CN})_8^{=}$, and $\text{Mo}_2\text{Cl}_7^{+4}$ are examples.

TUNGSTEN

This element was discovered by Scheele. He named it tungsten, which in the language of his native country means "heavy stone." The symbol, W, is derived from the German name of the element, *wolfram*, from *wolframite*, the principal ore of tungsten. This ore is essentially ferrous tungstate, FeWO_4 . Other tungstates also occur in minerals. It was from one of these, *scheelite*, that Scheele first prepared the element. This mineral is found in California. The world's supply of tungsten ores is produced from mines in China, Burma, and the United States (Colorado and California).

The ore is fused with sodium carbonate and the mass is leached with water. The solution obtained in this manner contains sodium tungstate, Na_2WO_4 . When this is acidified with HCl , tungstic acid, H_2WO_4 , is precipitated. The metal is prepared in the same way as molybdenum. As first prepared

the metal is hard and brittle but it is made malleable and ductile by pressing the powdered metal into rods and passing a current of electricity through them to fuse the particles. This treatment is followed by heat treatment and mechanical working of the metal, such as hammering and rolling, to give it the desired malleability and ductility required in different uses. The most important of these uses is the manufacture of the tungsten wires or filaments used in electric lamps. To make the small wires required for this purpose the tungsten is drawn through many diamond dies, each of which is smaller than the preceding one. Its high melting point (3370°) makes the metal extremely useful for this purpose, but since the metal is a good conductor, a very fine wire must be used so that the resistance will be sufficient to liberate enough heat to make the wire white-hot. Ferrotungsten is made by reducing wolframite with carbon and is used to make tungsten steels. These steels are strong and do not lose their temper when heated to redness. This property is useful in making cutting tools that are operated at very high speed, and which become very hot during their use. Tungsten steels are also used to make rails and many parts of the automobile, such as axles and steering apparatus. Tungsten is a constituent of many other alloys and is also used in making the targets or anti-cathodes of X-ray tubes, the filaments for radio tubes, phonograph needles, and contact points.

12. Chemical Properties and Compounds

In general, tungsten and its compounds closely resemble molybdenum and its compounds. In its compounds the metal has a positive valence of 2, 3, 4, 5, or 6. The divalent compounds are represented by such substances as WCl_2 and WBr_2 . These are usually prepared by the reduction of compounds in which tungsten has a higher valence. There are no simple compounds and only a few complex ones in which tungsten has a valence of 3. In its tetravalent state, the element forms the oxide, WO_2 , and the halides WCl_4 and WI_4 . The latter are strongly hydro-

lyzed, and the oxide is only very slightly basic in nature. The chloride WCl_5 is typical of pentavalent tungsten. This substance shows a strong tendency to form complex compounds. The most important compounds of the element are those in which tungsten is hexavalent. The trioxide, WO_3 , is the anhydride of tungstic acid, H_2WO_4 , and several condensed acids. The sodium salt of one of these is $Na_{10}W_{12}O_{41}$, which is the substance usually called sodium tungstate. The oxide also forms acids similar to phospho-molybdic acid. Phospho-tungstic acid, $H_3PO_4 \cdot 12 WO_3$ is used to precipitate proteins and alkaloids in the analytical chemistry of such substances.

The carbide of tungsten, W_2C , is almost as hard as diamond. When crystals of this substance are embedded in cobalt, a material is produced that may be used to make extremely hard cutting tools. These tools can be used to machine practically all metals, alloys, and other materials, such as glass, stone, and hard rubber. This material is best known under its trade name, *Carbalooy*.

URANIUM

This metal has been known as an element since 1789, when it was discovered in *pitchblende*, which contains the oxide U_3O_8 and the oxides and sulfides of several other elements. This mineral is found in Austria and in the Belgian Congo. Another uranium mineral called *carnotite* is found in Colorado and Utah. This is a potassium uranium vanadate, $K_2O \cdot 2 UO_3 \cdot V_2O_5 \cdot 3 H_2O$. The chief interest in these minerals lies in their radium content. For many years the chief source of radium and uranium was the pitchblende deposits of Austria. Later the carnotite deposits of Colorado superseded the Austrian source in importance, and these, in turn, were overshadowed by the production from the Belgian Congo.

The element, uranium, is prepared by the reduction of the oxide in an electric furnace. It is a white metal, which melts at about 1850° , and has a density of 18.7 g per cc. It is slowly oxidized in the air. It dissolves in the common acids, forming salts. The valence which it displays in its compounds is almost always 4 or 6. Lower valences are known, but the compounds in which

the element has these valences are not stable in aqueous solutions. The oxide, UO_2 , is basic, dissolving in acids to form green uranous salts, such as UCl_3 . The oxide, UO_3 , is amphoteric, forming uranates, which have the formula M_2UO_4 or $\text{M}_2\text{U}_2\text{O}_7$, or uranyl salts. The latter correspond to the base, $\text{UO}_2(\text{OH})_2$, which is uranyl hydroxide. The uranyl ion is divalent and its salts are such compounds as uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, uranyl aisenate, $(\text{UO}_2)_3(\text{AsO}_4)_2$, and uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$. The "oxide," U_3O_8 , is a compound, uranous uranate, $\text{UO}_2 \cdot 2\text{UO}_3$. Uranium compounds are used in coloring glass and glazes or in painting designs upon chinaware.

MANGANESE

13. Occurrence and History

Manganese is the only well-known element of Division A of group seven. Its most important ore is *pyrolusite*, MnO_2 , which is mined in Russia, Africa, India, and Brazil. A small amount is also produced in Georgia and in a few of the western states. It further occurs in the form of other oxides or hydrated oxides: *braunite*, Mn_2O_3 , *manganite*, $\text{MnO}(\text{OH})$ or $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$; and *hausmannite*, Mn_3O_4 . The carbonate and sulfide are also found. Before 1774, pyrolusite and magnetite (Fe_3O_4) were thought to be the same substance. In that year, Scheele proved that the two substances were distinctly different, and that pyrolusite was a compound of a new element. The name *manganese* is derived from a Latin word meaning *magnet*. The element is found in the combined state in many minerals containing iron, and in the soil from which it is removed by some kinds of plants. We are now obtaining some manganese ore from Cuba.

14. Preparation of the Metal, Its Physical Properties and Uses

Pure manganese has no commercial use and is difficult to prepare. It can be liberated from the dioxide or from other oxides by reduction with carbon in the electric furnace. The product contains carbon. More nearly pure manganese can be made by using pow-

dered aluminum as the reducing agent. Usually, alloys of iron and manganese are produced instead of the pure metal. These are made by the simultaneous reduction of manganese and iron ores in a blast furnace and are called *ferromanganese* and *spiegeleisen*. The former contains about 50 per cent of manganese and the latter about 20. These alloys are used in the production of steel either to remove impurities, such as oxygen and sulfur, or to make manganese steels, which contain from 10 to 15 per cent of manganese. These steels are very hard, but are more easily rolled and forged than manganese-free steels. They are strong and tough and are used wherever there is likely to be extensive wear, e.g. in steel rails and parts of machines. More than 90 per cent of the manganese ore produced in the world goes to make steel.

Manganese is a reddish-gray metal and in a very pure state is somewhat softer than iron. It melts at 1260° . If it contains carbon, it is very hard and brittle. It resembles iron in many of its physical and chemical properties.

In addition to its alloys with iron, manganese forms a number of important alloys with the nonferrous metals. *Manganese bronze* contains copper, manganese, tin, and zinc. It is especially resistant to the corrosive action of sea water and is used, for this reason, in propeller blades for steamships. *Manganin* is a brass containing manganese, copper, and nickel. This alloy is utilized as wire in making the coils for electrical resistance boxes, which are used in determining the resistances of other materials by comparison.

15. Chemical Properties and Compounds

Like iron, manganese is readily oxidized in the air if it is pure. The metal that contains carbon is more resistant to oxidation. It reacts slowly with water to liberate hydrogen and dissolves in acids, forming salts, such as MnCl_2 . The element forms five oxides and five corresponding series of salts. The five

oxides, then properties, and examples of the corresponding salts are shown in Table 44

16. Manganous Compounds

Manganous hydroxide is produced as a white precipitate when a soluble hydroxide is added to the solution of a manganous salt, e.g. MnCl_2 . This hydroxide dissolves in acids but not in hydroxide-bases such as NaOH . In the air it is rapidly oxidized to Mn_2O_3 , which is brown. Manganous chloride, MnCl_2 , and the sulfate, MnSO_4 , are the most important manganous compounds. They are stable in the air and are not readily oxidized.

17. Manganic Compounds

In its trivalent state manganese forms the hydroxide, Mn(OH)_3 , and corresponding manganic salts. These salts are very slightly stable and are easily reduced to manganous compounds. The hydroxide dissolves in acids but not in alkalis such as NaOH .

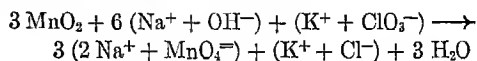
18. Tetravalent Manganese

The most important compound of tetravalent manganese is the dioxide, MnO_2 . This oxide is comparatively inert toward acids and alkalis. It does dissolve in cold concentrated hydrochloric acid to give a solution of MnCl_4 (green). At higher temperature manganese is reduced to Mn^{2+} and chlorine is liberated. The dioxide does

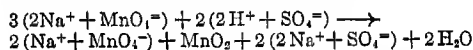
not dissolve readily in solutions of alkalis, but manganites can be produced by fusing the dioxide with the oxides of certain metals. These salts correspond to the purely hypothetical acid, H_2MnO_3 , or acids related to it. Calcium manganite, for example, is $\text{CaMn}_2\text{O}_6(\text{CaO} \cdot 2\text{MnO}_2)$.

19. Manganates (Hexavalent Manganese)

When any manganese compound, e.g. MnO_2 , is fused with potassium or sodium hydroxide or carbonate in the presence of potassium chlorate, lead dioxide, or some other vigorous oxidizing agent, a green mass is obtained



The green compound is an alkali manganate, e.g. Na_2MnO_4 . When water is added, this substance dissolves and is changed into permanganate and manganese dioxide. This reaction is more pronounced in the presence of acids



The production of green sodium manganate by fusion as described above is used as a means of identifying manganese in qualitative analysis.

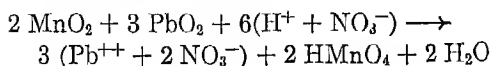
20. Permanganates (Heptavalent Manganese)

The most familiar and important compound of heptavalent manganese is potassium

TABLE 44
The Compounds of Manganese

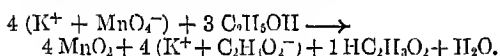
Oxide	Hydroxide	Properties	Salts	Color of ion
MnO	Mn(OH)_2	basic	MnCl_2 manganous chloride	pink
Mn_2O_3	Mn(OH)_3	basic	MnCl_3 manganic chloride	violet
MnO_2	Mn(OH)_4 H_2MnO_3	amphoteric (relatively inert)	MnCl_4 $\text{CaO} \cdot 2\text{MnO}_2$ (or CaMn_2O_6) calcium manganite	green
MnO_3	H_2MnO_4	acidic	Na_2MnO_4 sodium manganate	green
Mn_2O_7	HMnO_4	acidic	NaMnO_4 sodium permanganate	purple

sium permanganate, KMnO_4 . It is prepared as described in the preceding section of this chapter. A solution of the free acid, HMnO_4 , is prepared by treating lead dioxide and a manganous salt or manganese dioxide with a solution of hot nitric acid

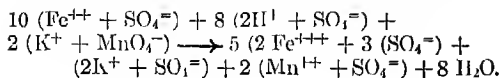


The solution of the acid is pink. This reaction is sometimes employed in the detection of manganese.

In previous chapters, several examples of the use of potassium permanganate as an oxidizing agent have been mentioned (page 328). In an acid solution the manganese is reduced to manganous ion, Mn^{++} , by such reducing agents as SO_2 , $\text{H}_2\text{C}_2\text{O}_4$, FeSO_4 , and H_2S . In a strongly alkaline solution the permanganate ion is reduced to manganate ion and, in the presence of a reducing agent, to MnO_2 or a hydrated form of this oxide. The following equation shows the oxidation of alcohol to acetic acid by potassium permanganate in an alkaline solution



Solutions of potassium permanganate are used in the laboratory to determine the amount of iron in a sample. The sample is first dissolved and ferric ions are reduced to ferrous ions by means of hydrogen or some other reducing agent that can be completely removed when this reaction is completed. A standard solution containing a definite concentration of KMnO_4 is then added from a burette to the solution of the ferrous salt



The permanganate solution is added as long as the solution is decolorized, and the volume of this solution required to completely oxidize the iron is read from the burette. From this volume, from the concentration of the solution of KMnO_4 , from the weight relations of KMnO_4 and FeSO_4 , as shown in the above equation, and from the volume of the solution containing the iron, the amount of iron in the sample can be calculated.

Potassium permanganate is used, also, in dyeing; as a disinfectant; as a bleaching agent, and in medicine for the treatment of ivy poisoning, snake bites, and other poisonous infections.

MASURIUM AND RHENIUM

These elements were discovered, in 1925, by means of the X-ray spectra (page 284) obtained in the examination of certain substances produced from ores containing platinum and other metals. They are also present in some of the ores of molybdenum and manganese. Masurium has not been produced in the pure state. Although the chemistry of these elements is not well known, it may be said that their compounds, in general, resemble those of manganese. Metallic rhenium can be produced in the same way as manganese, which it resembles in appearance and properties. It is extremely heavy and its melting point is above 3000° .

Masurium was produced, in 1937, by bombarding molybdenum with high-speed deuterons and neutrons. It has also been observed among the products of the fission of uranium (page 281). Recently, it has been renamed *technetium*.

Review Exercises

1. Construct a table showing the characteristic compounds of vanadium, columbium, and tantalum, and contrast these briefly with the compounds of nitrogen and phosphorus.
2. Enumerate the uses of the metals of the A division of group five and their compounds.
3. Construct a table showing the characteristic compounds of chromium, molybdenum, and tungsten, and contrast these with the compounds of sulfur.
4. Describe the occurrences of chromium in nature, the methods of producing it from its ores, and its uses.
5. What is ferrochrome and for what purpose is it used?
6. Starting with the most abundant ore of chromium outline a method by which potas-

- sum dichromate can be produced. Write all equations for the reactions.
7. A sample of potassium dichromate was added to a solution containing HCl . Assuming that the reaction was complete, what weight of the dichromate was added, if the volume of the chlorine liberated was 150 ml. (standard)?
 8. Write a balanced equation to show the reaction of potassium dichromate with hydrogen sulfide in an acid solution (H_2SO_4), if the sulfur is liberated as the free element.
 9. In which of its compounds does manganese most closely resemble chlorine?
 10. A sample of non ore weighing 0.1 g. was dissolved in 100 ml. of a sulfamic acid solution, and the non was completely reduced to Fe^{++} . Twenty-five ml. of the solution was then titrated, requiring 5 ml. of a solution containing 1 g. of potassium permanganate per liter. What was the percentage of non in the ore sample?
 11. How would you prepare potassium permanganate from manganese dioxide?

References for Further Reading

- Evans, U. R., *Metals and Metallic Compounds*, vol. II, page 301
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METALS OF GROUP EIGHT

THE elements of group eight consist of three series of metals (1) iron, cobalt, and nickel, (2) ruthenium, rhodium, and palladium, and (3) osmium, iridium, and platinum. Each of these series lies in the middle of one of the long periods of elements in the periodic classification. The metals of the first series are much more abundant and important than those of the second and third. They are also relatively active metals, while the others are noble metals similar to platinum. Iron, cobalt, and nickel closely resemble one another, with cobalt resembling iron somewhat more closely than nickel does. The atomic weights of these metals (Fe, 55.84, Co, 58.94, Ni, 58.69) are much closer together than is generally true of other groups of related elements in the periodic table.

All of the elements of group eight are metallic and form compounds in which they have positive valences of 2 and 3. The metals of the second and third series may also be quadrivalent, and in a very few compounds a valence of 8 is indicated. Some of these elements form compounds in which they act as non-metals. Examples of such compounds are found in the chemistry of iron, which forms ferrites and ferrates.

IRON

1. History and Importance

The first metallic articles made by man were probably made of bronze, but iron was known as long ago as 4000 B.C. and probably has been used to some extent since very early times. The symbol, Fe, of the element and the names of its compounds, *ferrous* and

ferric, are derived from the Latin name *ferrum*. The iron first used by man was probably of meteoric origin. Primitive methods of smelting iron ores consisted in mixing the ores with charcoal and covering over a pile of this material with clay. A hole was left at the top and one at the bottom to produce a draft. The charcoal was ignited, and some of it burned, liberating heat that raised the temperature of the mass. Carbon and carbon monoxide reduced the iron oxide. The production and use of iron on a large scale began about 1620, when the ores of the metal were first reduced by means of coal.

Iron is the most widely used and important metal. Its position of importance is due to at least three factors: (1) the ores of the metal are abundant, contain large percentages of iron, and are found in many parts of the world, (2) the metal is easily and cheaply produced from its different ores, and (3) the properties of the metal can be varied over a wide range by different methods of treatment or by the addition of other substances, thus producing metal adapted to many widely different uses. To most persons the name metal is almost synonymous with iron, and the most casual observer is aware of the fact that more iron is used than all of the other metals together.

2 Occurrence

The principal ores of iron are *hematite*, Fe_2O_3 , *limonite*, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; *magnetite*, $\text{Fe}_3\text{O}_4(\text{FeO} \cdot \text{Fe}_2\text{O}_3)$, *siderite*, FeCO_3 , and *pyrite*, FeS_2 . Hematite is the most important of these ores. The Lake Superior region

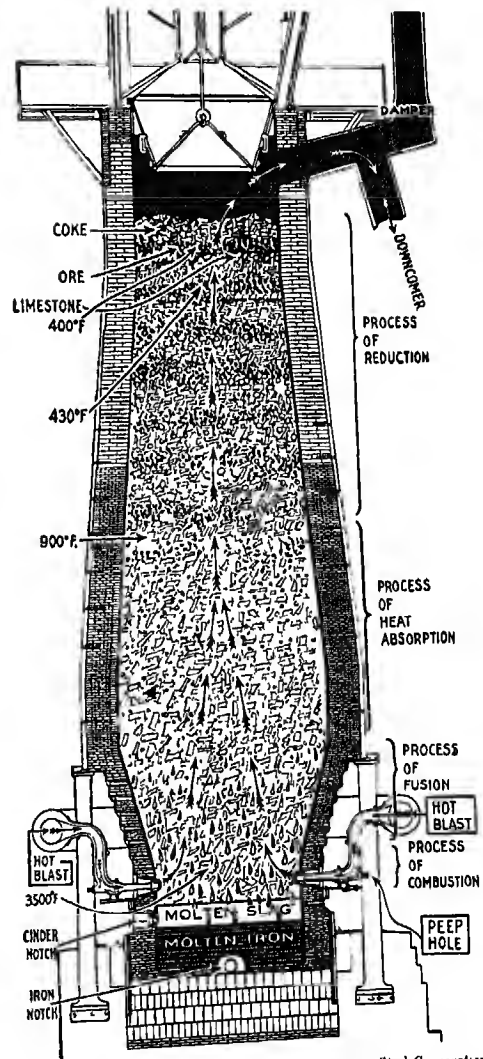
furnishes more than 80 per cent of the ore mined in the United States. The second most important iron-ore mines in this country, at the present time, are in the region around Birmingham, Alabama. Other deposits are located in California, Colorado, and New York. The other principal producing countries are France, Great Britain, Germany, Russia, Canada, and Sweden. Iron compounds occur in almost all rocks and soils, adding much of the coloring of many formations. Iron is also found in the chlorophyll of plants and in the hemoglobin of the blood, and appears to be necessary for the proper functioning of these substances and to life itself. The raw materials used in producing iron, in addition to the iron ore itself, are coke and limestone. Hence, iron and steel plants must be located near sources of coal and limestone, and also with the idea of securing low transportation rates for the ore. In the United States, Pittsburgh is admirably located as an iron and steel center. It is near deposits of coal and limestone and the cost of transporting these materials is consequently minimized. It is also only a relatively short distance by rail from ports on Lake Erie, to which the ore is carried from the Lake Superior region on large ore boats, designed for rapid loading and unloading at a very small cost. The growth of the steel industry in Gary, Indiana, is also due to its favorable location with respect to the transportation of iron ore over routes on the Great Lakes.

METALLURGY OF IRON AND STEEL

3. The Blast Furnace

Iron ores are reduced in a blast furnace (Figure 319). This is a steel tower, about 100 feet in height, and 20–22 feet in diameter at the widest point. It is lined with fire brick, and the walls of the lower part of the furnace are cooled by water which circulates through blocks or tubes made of bronze

and embedded in the walls. The furnace tapers toward the top and toward the bottom. The lower constriction in the size of the tower is necessary to provide a support for the charge, when the materials near the bottom of the furnace melt. A blast of hot air is blown into the furnace, near the bottom, through pipes which are called *tuyeres*. The charge consists of suitable proportions of ore, coke, and limestone. This material is dumped from cars into the top of the



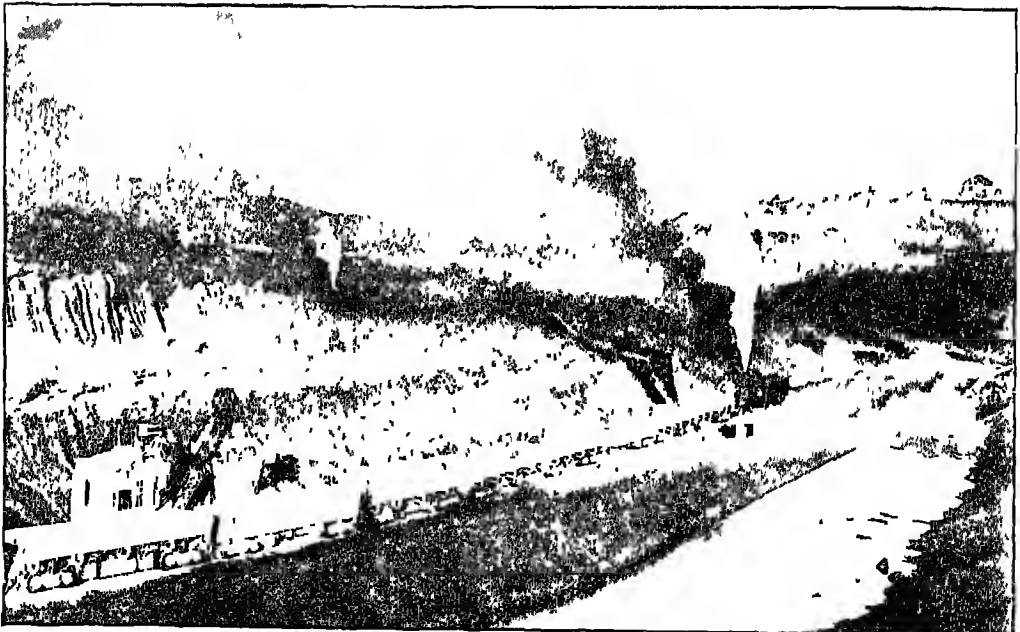
Courtesy of United States Steel Corporation

Figure 319 Cross Section Diagram of a Blast Furnace

furnace through a trap called a *bell*. This arrangement is intended to prevent the furnace from remaining open at the top, thus causing a strong draft which would remove the gases in the furnace too rapidly and also lower the temperature. The gases are led off through a pipe at the top. Since they contain carbon monoxide, they have some value as fuel. They are burned to heat the air which is blown into the furnace through the tuyeres and to supply the energy required for the operation of machinery in other parts of the plant. Coke is added for two purposes. Its combustion in the lower part of the furnace provides the heat which is required for the process and which serves to melt the iron and slag which are produced. It also acts as the reducing agent or produces carbon monoxide, which acts in this capacity. The limestone is added as a flux. Most iron ores contain silica and clay which must be separated from the iron. The limestone reacts with these substances to produce a slag, which melts in the lower portion of the furnace and floats on top of the liquid iron.

It is drawn off, as it collects, through a conduit. If the iron ore is very pure, both silica and limestone must be added to form a slag, which is a necessary product of the process. The slag serves the following purposes. (1) it collects on top of the iron and provides a protection against oxidation, which otherwise would be very rapid at the temperature existing in the lower part of the furnace, (2) the liquid slag provides a medium in which the melted iron, which is produced in small drops, may collect into a single mass. The second condition is essential, since the melted iron could not be easily collected if it were formed in the presence of solid materials. The melted iron collects in the lowest part of the furnace, which is called the *crucible*. The narrow portion of the furnace above the crucible is called the *bosh*. The operation of the furnace is continuous, iron is removed about every six hours.

Several reactions occur in the furnace but each reaction is fairly simple. The air that enters the furnace near the top of the crucible, or at the bottom of the bosh, burns



Courtesy of United States Steel Corporation

Figure 320 Production of Iron Ore in the Mesabi Range of the Lake Superior Region

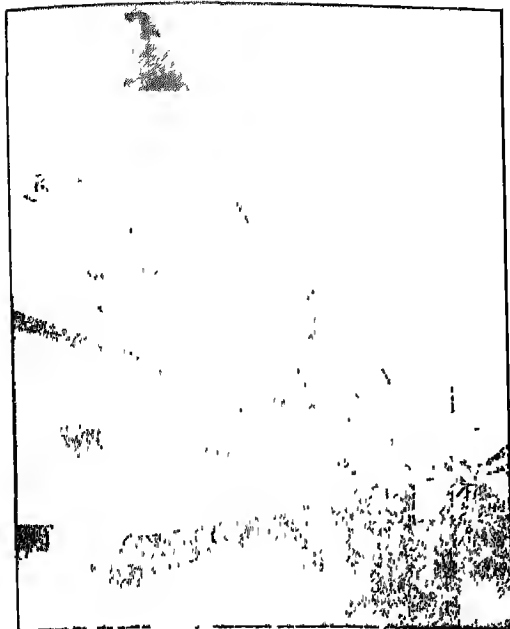
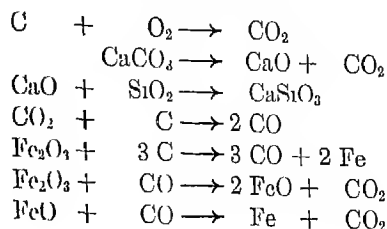


Figure 321 Blast Furnaces

Each of the three furnaces has a daily capacity of 1120 tons of pig iron

some of the fuel, forming carbon dioxide. The temperature at this point is about 1900° . At the top of the bosh, where the temperature is about 1500° , the limestone is decomposed, forming CaO and liberating more CO_2 . Here and at lower levels the lime and silica react to form the slag. Here, too, some of the iron ore, which has escaped reduction in the upper part of the furnace is reduced by the direct action of carbon. The carbon dioxide passes with other gases up through the charge, and slightly above the top of the bosh it is reduced to carbon monoxide, which acts as the reducing agent in the upper portion of the furnace. The temperature near the top is about 300° . In this region the carbon monoxide probably reduces the ore largely to ferrous oxide, FeO , and the reduction to the metal is completed in the lower portion of the furnace, where the temperature is above 500° . An excess of carbon monoxide is necessary to produce a reducing atmosphere and to prevent the

oxidation of iron by carbon dioxide. The reactions are summarized below



The slag which comes from the blast furnace may be used in the manufacture of Portland cement (page 664). The iron which is drawn off as a liquid from the crucible is run off into large buckets for transportation to the steel mill or into molds or troughs and cast into forms called "pigs." Pig iron is then used as the starting material in the production of all varieties of iron and steel. It contains 2.5 to 5 per cent of carbon and varying small amounts of silicon (about 2 per cent), manganese, phosphorus, and sulfur. It must be refined before it can be used for almost all purposes, since it has a very low tensile strength and is brittle. The production of pig iron fluctuates from year to year with the periods of prosperity and depression in the business world. The producing capacity of the United States is estimated at about 100,000,000 tons. A single blast furnace produces 500 to 1100 tons of iron per day. In some countries, where hydroelectric power is cheap, iron ores are reduced in electrically heated furnaces.

4 Cast Iron

This is the nearest relative of pig iron. It is made by melting the latter in a *cupola furnace* with scrap iron of somewhat better quality than the pigs themselves. The furnace is much smaller than a blast furnace but has about the same design. Coke is added as the fuel and some additions, such as ferromanganese, may be made. The liquid iron is cast in sand molds, in which it is cooled gradually. The product is called *gray cast iron*. It always contains about 4

per cent of carbon and variable amounts of silicon and manganese, with smaller amounts of sulfur, phosphorus, and other elements. It cannot be welded, rolled, or forged, and has a small tensile strength. It is used largely in producing articles that can be made by casting instead of forging or machining — articles such as the parts of stoves and steam radiators. The carbon contained in gray cast iron is present largely as a carbide, Fe_3C , called *cementite*, which decomposes and liberates carbon as graphite as the iron cools slowly, graphite is responsible, in considerable measure, for the color and other properties of the metal. *Chilled or white cast iron* is made by rapidly cooling the iron, or at least the surface portions, while it is in the molds. This variety of cast iron contains carbon in the form of cementite rather than graphite. It is very hard and brittle, and possesses excellent wear-resistance. *Malleable cast iron* is made by heating white cast iron for 50 to 70 hours at a red heat and then allowing it to cool gradually. Most of the carbon in this product is present as small particles of graphite. This variety of cast iron is slightly more desirable in making the parts of heavy machines and certain kinds of tools and implements. It is fairly strong but it cannot be welded or forged.

5 Wrought Iron

Wrought iron is a fairly pure form of iron made by burning out most of the impurities that occur in the product of the blast furnace. The process is carried out in a *puddling*

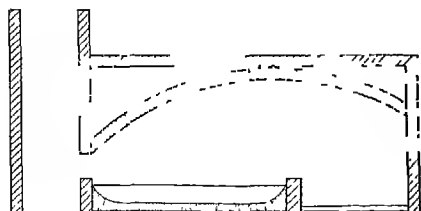


Figure 322 Puddling Furnace

furnace, which is a small reverberatory furnace (Figure 322). The heat is reflected from the roof of the furnace upon the charge, which consists of pig iron on top and a layer of iron oxide on the bottom. The iron melts and the impurities are oxidized by the oxide. The carbon and sulfur are removed as carbon dioxide and sulfur dioxide. Silicon and phosphorus are changed into oxides. These react with oxides of iron and manganese or with limestone, which may be added as a flux, to produce a slag. The more nearly pure iron which is formed, as the impurities are removed, has a higher melting point than pig iron, and the mass consequently becomes less fluid. It is raked together by means of a "rabble" and removed from the furnace in large balls. These are hammered or rolled to remove the slag. The product contains 0.2 per cent or less of carbon. It is fibrous and is softer and stronger than cast iron but not so strong as steel. It is malleable and ductile. It is used to make articles which can be hammered into shape while red hot, plowshares, anchors, and horseshoes are examples. Wrought iron has been replaced in recent years to a large extent by steels containing very small amounts of carbon.

STEEL

The term *steel* is a name which is applied to many widely different alloys of iron. It is made from pig iron by burning out the impurities and later adding constituents such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce steels which possess specific properties and which are suited for specific uses. Steels usually contain between 0.1 and 1.5 per cent of carbon. Hence, a large part of the carbon contained in pig iron must be removed in the production of steel. Phosphorus, silicon, and sulfur, which are especially objectionable because they make steel brittle, must also be largely removed. The two most generally used methods of making steel are the *Bessemer* and the *Open-Hearth* processes.

6. The Bessemer Process

This process depends essentially upon the use of an air blast in burning the impurities out of pig iron. It is named after the Englishman, Bessemer, to whom an English patent for the process was granted in 1855. The reaction is carried out in a large egg-shaped crucible (Figure 323), called a Bessemer converter. The crucible is made of steel, and in the United States is usually lined with silica brick. The silica constitutes an "acid" lining, which will react with basic oxides that are produced by the oxidation of the impurities but not with the oxides of phosphorus or sulfur. Hence, the *acid*-Bessemer process is suited only to the production of steels from pig iron containing inappreciable quantities of these two elements. If much phosphorus is present in the iron, a converter lined with dolomite brick, which is basic, may be used.

The converter is built on a trunnion so that it may be tipped over to receive the charge of melted iron from the blast furnace, or to deliver the finished product into large ladles. A converter holds from 15 to 25 tons of steel. Air is forced under a pressure of about 30 pounds through a hollow trun-

nion into an air box in the bottom of the converter. From here the air passes through holes in a false bottom of the converter into the liquid mass of the charge. The oxidation of the impurities, especially the oxidation of silicon, liberates considerable heat, and during the "blow," flames and sparks are shot out of the mouth of the crucible with a dazzling, blinding brilliancy. The oxides of manganese and iron react with the silica to form a slag that floats on top of the molten iron. The air blast is continued until the character of the flame indicates that the carbon is completely oxidized. The time of a blow is 10 to 20 minutes. Carbon, manganese, chromium, and other elements are then added to give a product of the desired composition. These elements usually are added in the form of iron alloys, such as ferromanganese or Spiegeleisen, which contain a known quantity of carbon. To remove oxygen which may remain in the steel, or which may become trapped in it as the metal is poured, deoxidizers are also added prior to pouring. Aluminum, ferromanganese, or ferrosilicon are used for this purpose. If not removed, the gas would form small bubbles which would weaken the steel. The converter is tilted and the charge is poured into large ladles and then into large molds where it solidifies in the form of ingots. The ingots are rolled to make rails or hammered into other articles.

In America, the use of the acid-Bessemer process is limited because it does not remove phosphorus and sulfur. The steel made by this method is usually considered somewhat inferior to that made by the open-hearth process and more likely to contain flaws. Bessemer steel is used largely to make railroad rails and the steel frameworks of buildings, bridges, and other structures. Another disadvantage of the process is the rapidity with which it must be operated. In order to prevent the iron from oxidizing, the air blast must be discontinued as soon as the impurities are burned out, and the iron must then be poured immediately before

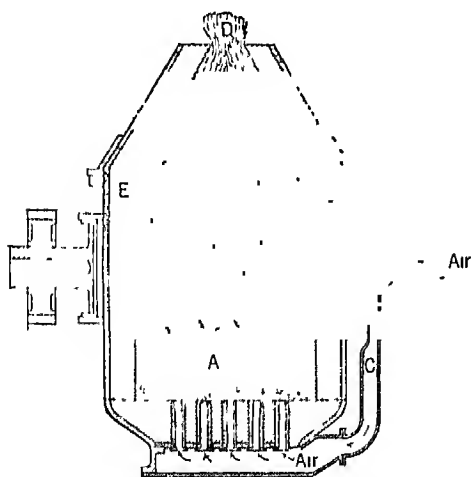
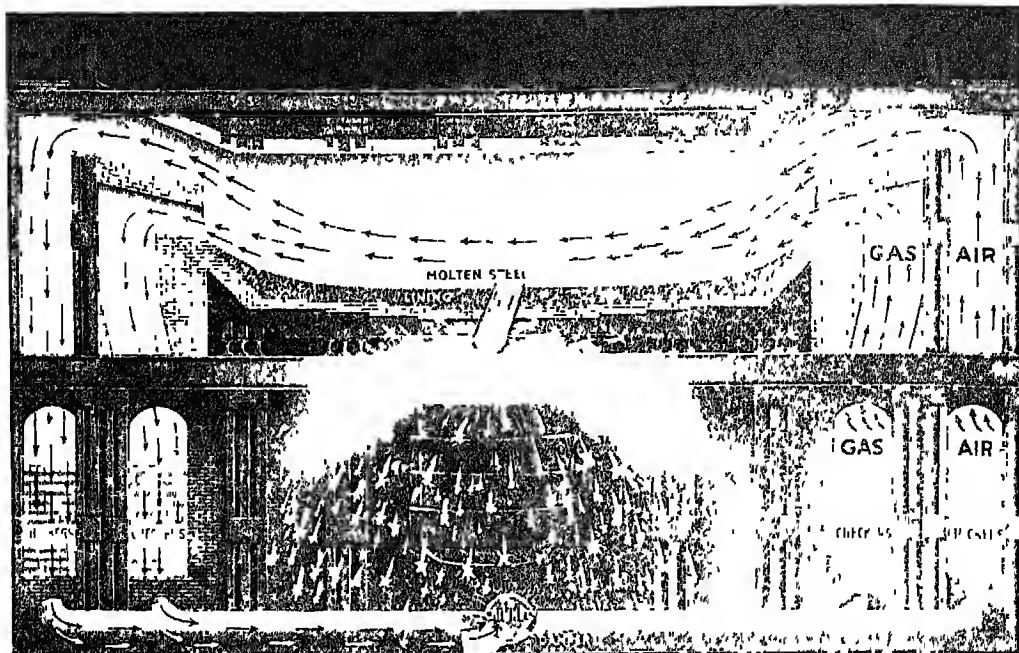


Figure 323 The Bessemer Converter

Air enters the converter (E) through the trunnion (B). Gases resulting from the combustion of impurities escape at D and the molten steel collects at A.



Courtesy of United States Steel Corporation

Figure 324 Open-Hearth Process of Steel Making

Molten steel lies about 24 inches deep on a bed about 40 feet long by 16 feet wide. The lining of this bed consists of magnesite, dolomite, and lime. The walls and roof are constructed of silica bricks. The illustration shows the current of hot gas and air being forced above and around the molten metal and passing out through the checkers at the left, and from there out to the chimney. Ore of less purity than that used in the Bessemer process is successfully made into fine steel by the open-hearth process.

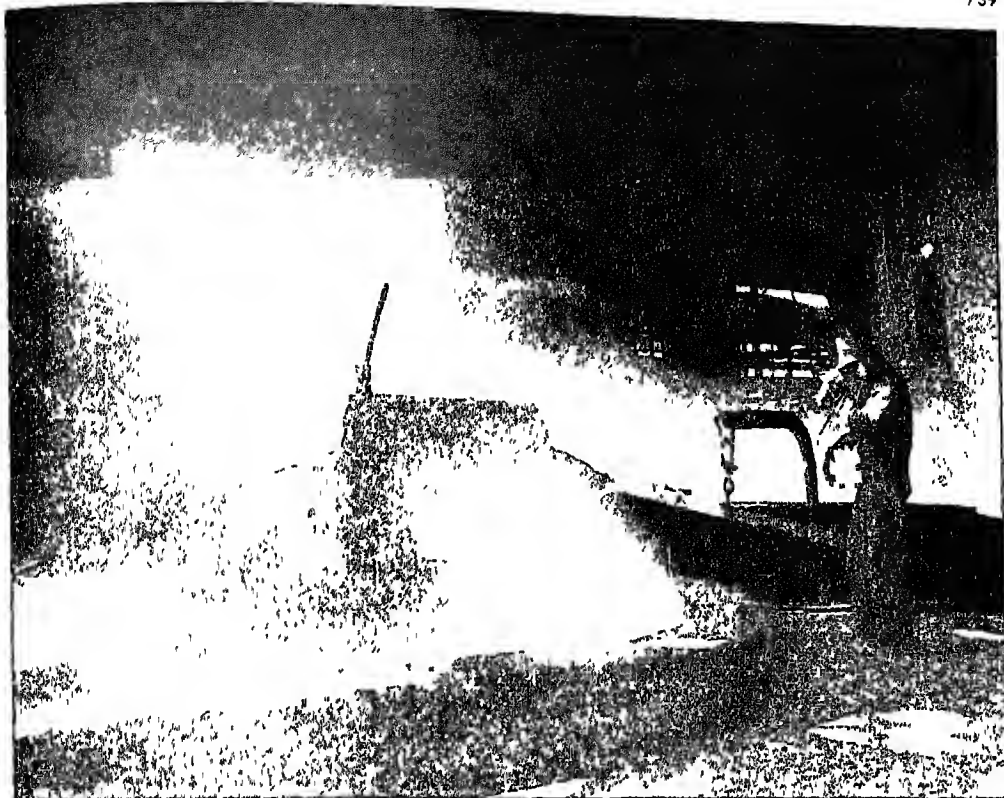
it has a chance to solidify. It has the advantage of lower costs, however, over the open-hearth process.

7. The Open-Hearth Process

The furnace used in this process is shown in Figure 324. A charge consisting of pig iron, iron ore, scrap iron covered with rust, and limestone is placed on the furnace hearth. The hearth of the furnace is usually made of a basic material, such as limestone, dolomite, or magnesite. A hearth made of silica brick is used in the acid open-hearth furnace to make steel from iron which contains very little phosphorus or from scrap steel. Heat is provided by burning fuel gas, an oil spray, or powdered coal over the charge. The fuel and air enter through preheaters. The air is preheated by passing through a brick-work chamber before it enters the furnace. If a gas is used as fuel

it may be preheated in a similar manner. The hot gases produced during the oxidation of the carbon, sulfur, and certain other impurities pass off through another brick-work chamber. The directions of the entering gases and the gaseous products are reversed frequently so that each chamber is alternately heated and serves, in its turn, to preheat the air. The carbon is removed from the iron as carbon dioxide, while the phosphorus, sulfur, and silicon are converted first into oxides and then into fusible compounds by interaction with lime or magnesia. This material collects as slag on the surface of the steel and is easily removed. The furnace makes about 50 tons of steel at one time. The process requires about 12 hours for each charge.

Near the end of the reaction deoxidizers are added. Because the process is very slow, the steel can be analyzed from time to time,



Courtesy of J. I. Lott

Figure 325 Tapping a Blast Furnace

and the operation can be stopped when the analysis shows that the desired carbon content has been reached. Just before the steel is poured, the required and calculated amounts of manganese, chromium, and other elements are added.

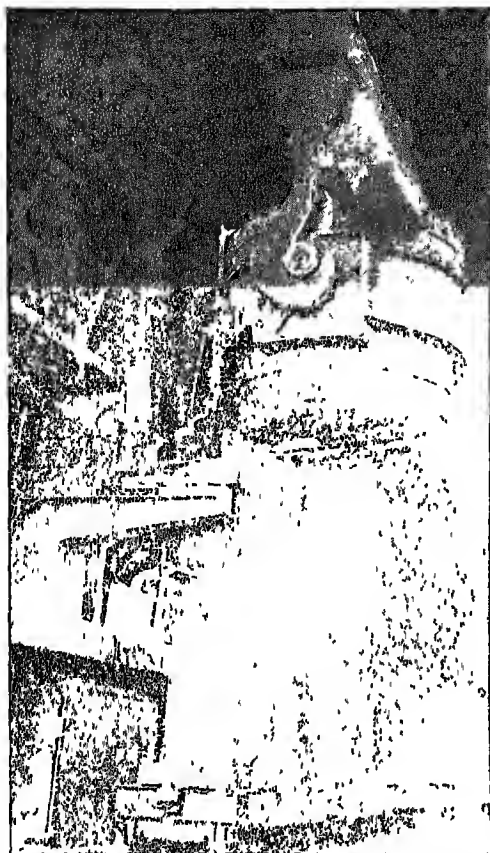
After the removal of the slag, molten steel is poured by allowing it to run into ladles (actually large buckets). Sometimes oxygen scavengers and elements that form alloy steels are added to the charge in the ladles. From the ladles the steel is poured into molds to form ingots. Blowholes, produced largely by carbon monoxide, may form as the ingots solidify. These can be prevented by adding scavengers that combine with oxygen and thus prevent the formation of carbon monoxide. Blowholes are also removed by rolling and drawing.

Slightly more than 90 per cent of the steel

made in the United States is produced by the basic open-hearth process. Open-hearth steel is uniform in structure and is less likely to contain flaws than Bessemer steel. Some steel is produced in electric furnaces, which operate on the same principles in producing steel as the open-hearth furnaces, except for the use of electricity as a source of heat. The use of the electric furnace in steel manufacture is increasing but is still limited. About 2 per cent of all steel and above 20 per cent of the alloy steels are produced in such furnaces.

8. Crucible Steel

High-grade steel, containing up to 1.5 per cent of carbon, is made by melting the steel from the Bessemer converter or the open hearth in large crucibles. The required amounts of carbon and other elements



Courtesy of United States Steel Corporation

Figure 326 Pouring Steel into Ingot Molds

(chromium, manganese, tungsten, etc.) are added and allowed to dissolve in, or alloy with, the iron. The steel made in this manner has a uniformly high quality. It is used mainly in the manufacture of tools and of articles such as springs, files, razor blades, and knives.

9 Hardening and Tempering Methods

Steel ingots, after they have solidified, are placed in a soaking pit. Here they are kept at red heat for some time in order that the strains and stresses produced during solidification may be relieved. Afterwards, while still hot, the steel goes to the rolling mill where it is rolled, that is, worked into different shapes by being passed through steel

rollers. Some may be drawn into wire or rod, and some may be forged.

The properties of iron and steel depend, to a considerable extent, upon the physical state of the iron and upon the condition of the carbon. At ordinary temperatures, the stable form of iron is soft. This is called *alpha iron* or *ferrite*. At temperatures above 900° , this modification of iron changes to *gamma iron*, which consequently is the form of iron in steels that are heated to high temperatures for some time. This form of iron dissolves carbon up to about 1.5 to 2 per cent, and when rapidly cooled, crystallizes to give a solid solution of *cementite*, Fe_3C , and *gamma iron*. This solution is called *austenite*. Steel of this composition is made by quenching the hot metal in water or oil. The composition remains unchanged during the cooling, since the change to *alpha iron* and the changes involving carbon do not have time to occur. This steel is hard and brittle. If steel is cooled slowly, the *alpha* modification of iron is produced, and the carbon is largely deposited as segregated crystals of *cementite* or as particles of graphite. This variety of steel is softer, more pliable, and has a higher tensile strength than steel which has been cooled rapidly.

If steel which has been cooled rapidly is reheated to temperatures between 200° and 325° , some changes occur in the composition, and the properties of the steel are modified accordingly. The solid solution of *cementite* and iron is broken up to some extent by the crystallization of segregated *cementite* or graphite. At the same time, some of the mechanical strains resulting from rapid cooling are also relieved. By varying the temperature, the length of the period of heating, and the rate of cooling, these changes may be made to occur to different extents, and steels possessing varying degrees of hardness can be produced.

Case-hardened steel is made by heating low-carbon steel in closed containers with powdered carbon and later quenching it in oil. The steel takes up some of the carbon on its

TABLE 45

Alloy Steels

Element	Percentage	Properties of Steel
Silicon	1 - 2 12 - 15 (Duriron)	Hard, strong Resistant to corrosion, acids, etc
Cerium	70	Pyrotechnic, emits sparks when scratched
Nickel	1.5 - 4	Strong, resistant to corrosion, tough, low coefficient of expansion
Nickel-Chromium	1 - 1.5 and 0.2 to 0.7 7 - 10 and 18	Hard, tough, high tensile strength
Chromium	1.5 - 5 10 - 15	Stainless, strong Hard, strong, tough
Vanadium	0.1	Stainless Tough
Manganese	10 - 14	Hard, resistant, strong, tough
Tungsten	4 - 18	Hard, holds temper when heated.
Carbon	0.1 - 1.5	Hard
Molybdenum	6 - 7	Holds temper when heated
Lead	1 pt in 500	Easily machined
Titanium	0.1	Very hard

surface, thus producing a metal which has a thin layer of hard high-carbon steel on its surface and a core of strong, pliable, low-carbon steel. Steel treated in this manner is used to make axles, car wheels, and other articles that must be hard to resist wear and, at the same time, somewhat flexible to prevent breaking when subjected to sudden strains and shocks. A similar variety of steel is made by heating the metal in an atmosphere of ammonia. In this case the surface is hardened by the formation of iron nitride.

10 Alloy Steels

Some of the materials added to iron in the manufacture of steel act as purifiers or scavengers. Aluminum, silicon, titanium, and manganese are often added for this purpose. These substances insure the complete reduction of any iron oxide that might otherwise escape reduction. They react with available oxygen to form very stable oxides, thus preventing the formation of carbon monoxide, which would produce blowholes in the steel. The compounds formed by the oxidation of the scavengers are removed in the slag.

Other elements, usually metals, are also added. These remain in the steel and form alloys with the iron. The simplest steels contain small percentages of carbon and manganese. In order that steels may be produced that are hard and, at the same time, strong instead of brittle, chromium, nickel, manganese, vanadium, molybdenum, silicon, manganese, and niobium are added. For every ton of steel produced about 30 pounds of non-ferrous metals are added or used as coatings. By varying the number and percentages of these elements, it is possible to produce steel possessing practically any set of properties. Frequent mention of such steels has been made in discussing the chemistry of other metals. The composition and the important features of a few of these steels are summarized in Table 45. The percentages of the added elements vary considerably, and those given should be considered as typical of a few common alloys.

11. Properties of Pure Iron

Pure iron is scarcely ever prepared on a commercial scale and is not well known even in the laboratory. It may be made by re-

ducing pure ferric oxide with hydrogen and heating the product for some time in a vacuum to remove adsorbed hydrogen. It is also made by electrolysis, using iron electrodes and ferrous sulfate as the electrolyte. Wrought iron comes the nearest of the commercial forms of iron to possessing the properties of the pure metal. Pure iron melts at about 1530° , wrought iron at about 1500° , and pig iron at about 1100° . The pure metal has a silvery-white luster, and is malleable, ductile, and relatively soft. It possesses much stronger magnetic properties than any of the commercial forms of iron. Two of its allotropic modifications, alpha iron and gamma iron, have been mentioned in connection with the tempering of steel (page 740). In addition to these there is a third form, *delta iron*, which is stable above 1400° .

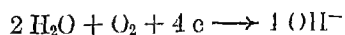
Chemically, iron is a relatively active metal. In this connection, the displacement of hydrogen from steam by hot iron, the burning of finely divided iron in air and in oxygen, its direct combination with sulfur and with moist chlorine, and its displacement of hydrogen from hydrochloric and sulfuric acids will be recalled as examples of its activity. Like some of the other metals (page 722) iron has a passive state, and when in this condition it does not react with dilute acids. It is made passive, for example, when it is dipped in fuming nitric acid. It becomes active again when it is scratched or struck. Iron forms two series of compounds in which it has a valence of positive 2 and positive 3, respectively. Its oxides and hydroxides are basic. Iron forms a few compounds in which its valence is apparently 4, e.g. BaFeO_3 , and others in which the valence is 6, e.g. Na_2FeO_4 . These compounds show that iron has a slight tendency to act in the same way that aluminum, zinc, lead, and other amphoteric metals act. These compounds are of little importance.

12 The Corrosion of Iron

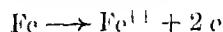
The corrosion, or rusting, of pure iron is slow. Impure iron corrodes more rapidly

but only in the presence of moisture. In pure water the reaction is slow, but solutions of electrolytes cause rapid corrosion.

Corrosion is probably the result of electrolysis. Metals higher in the electrochemical series than iron act as the cathode. Wherever they are located — as impurities in the iron — water molecules react with oxygen (dissolved) and remove electrons from the cathodes to form hydroxyl ions



Iron, itself, acts as the anode, at which iron is converted into ferrous ions



Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, is thus formed and is readily oxidized to $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$, hydrated ferric oxide, which is the principal component of iron rust. The water content of this compound varies, and therefore the number of molecules of water in the hydrate is represented by x . Because the reaction is one involving electrolysis, a solution of an electrolyte causes more rapid corrosion than pure water. The electrolyte is often only a solution of carbon dioxide (carbonic acid).

To protect iron from corrosion, it may be painted, alloyed with other metals, treated while hot with steam, which forms a protecting coat of Fe_3O_4 on the surface, covered with oil or grease, which excludes oxygen and water, or covered with a metal, as in tin plate or galvanized iron.

13 Oxides and Hydroxides of Iron

Ferrous oxide, FeO , is a black powder. It can be made by reducing ferric oxide with hydrogen at a temperature of 300° or lower, or by the decomposition of ferrous oxalate, FeC_2O_4 . The corresponding hydroxide, $\text{Fe}(\text{OH})_2$, is a white solid which may be precipitated by adding a soluble hydroxide to a solution of a ferrous salt. It tends to become a colloidal gel, resembling aluminum hydroxide in this respect. When allowed to stand in contact with the air, it turns green and

then brown as it is oxidized to hydrated ferric oxide or $\text{Fe}(\text{OH})_3$.

Ferric oxide, Fe_2O_3 , is prepared by igniting ferric hydroxide, $\text{Fe}(\text{OH})_3$, or by roasting pyrite, FeS_2 , in the air. It is an insoluble red powder. It occurs in nature as the important mineral hematite, which varies in color from brownish-red to black. Iron rust and the iron ore, limonite, contain hydrated forms of the oxide, of which $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ are typical.

Very pure, gutless ferric oxide is used commercially as jeweler's *rouge* and as *Venetian red*. As the latter it is used as a pigment in paints for barns, bridges, railway cars, etc., and as a pigment for pottery and rubber. Ferric hydroxide is precipitated as a reddish-brown gel when a soluble hydroxide is added to a solution of a ferric salt. This substance, although usually assigned the formula $\text{Fe}(\text{OH})_3$, is probably a mixture of the hydrated forms of ferric oxide. The precipitate dissolves in acids but not in solutions of bases.

The two oxides of iron are found together in nature as the mineral *maghemite*, Fe_3O_4 . This substance is a compound whose composition is best represented by the formula Fe_2FeO_4 . This compound is sometimes found on the surface of iron that is heated in the air. It forms a durable, tightly adhering, and non-porous film on the object and protects it against rusting. Such a film is found on gun barrels.

14 Ferrous Sulfate, FeSO_4

The most widely used ferrous salt is the *sulfate*, FeSO_4 . It is prepared by dissolving iron in dilute sulfuric acid and evaporating the solution. Scrap iron may be used for this purpose, and a considerable quantity of commercial ferrous sulfate is recovered from the pickling baths in which sheet iron is dipped before it is galvanized or coated with enamel. Ferrous sulfate is also prepared by the oxidation of moistened pyrite in the air. The ferrous sulfate is later extracted from the mass with water. The salt crystallizes from solution as the green hydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$,

which is called *green vitriol*. The crystals lose the water of hydration when exposed to the air and become brown in color due to the oxidation of the ferrous sulfate. Solutions of the salts are not permanent, since the ferrous sulfate is readily oxidized to $\text{Fe}(\text{OH})\text{SO}_4$, the basic ferric sulfate. To prevent this change, the solution is acidified with sulfuric acid and kept in contact with metallic iron. Ferrous sulfate is used in the purification of water, where it acts in the same manner as aluminum sulfate (page 179). It is also used in medicine, as a disinfectant, as a weed killer and wood preservative, in the manufacture of black inks and dyes, and as a reducing agent in the laboratory and in commercial operations. When used in inks, tannin is also added. This reacts with ferrous sulfate to form the ferrous salt of tannic acid. This salt is oxidized to ferric tannate, which is black, but this change is prevented in the ink by the addition of sulfuric acid and a protective colloid, such as gum arabic. A blue dye is added to give the ink a color when it is first used in writing. After standing on the paper for some time, the ferrous tannate is oxidized to the black ferric salt.

Bluish-green crystals of the double salt, *ferrous ammonium sulfate*, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, separate from a solution containing equimolecular amounts of ammonium and ferrous sulfates. This substance is stable in the air, and for this reason is preferable to ferrous sulfate in analytical chemistry.

15 Ferrous Chloride, FeCl_2

This salt crystallizes as the hydrate, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, from solutions made by dissolving iron in hydrochloric acid. The crystals of the pure, hydrated salt are blue, but they turn green in the air as oxidation progresses. The anhydrous salt is prepared by the action of hydrogen chloride upon iron. The salt is used as a reducing agent and, in a limited way, as a mordant.

16 Other Ferrous Compounds

Ferrous sulfide, FeS , from which hydrogen

sulfide is prepared, is made by heating iron filings with sulfur. It is precipitated as a black compound, when hydrogen sulfide is passed into an alkaline solution of a ferrous salt. Natural ferrous sulfide is called *pyrrhotite*. *Ferrous carbonate*, FeCO_3 , occurs in nature as *siderite*, and may be precipitated from solutions of ferrous salts by soluble carbonates. It is soluble in the presence of an excess of carbon dioxide because, like calcium carbonate, it forms the bicarbonate $\text{Fe}(\text{HCO}_3)_2$. Water which comes from beneath the surface of the earth frequently contains the bicarbonate in solution and is called *chalybeate water*. When it reaches the air, carbon dioxide is lost, and FeCO_3 is first produced. By a series of reactions involving oxidation and hydrolysis, the iron is finally deposited as ferric hydroxide or hydrated ferric oxide.

17 Ferric Chloride, FeCl_3

This is the most important ferric salt. It is made by the action of chlorine upon iron. This reaction gives the anhydrous salt as black crystals. The salt can be sublimed when heated. It is very soluble in water and forms several hydrates. The most familiar hydrate, from which solutions of ferric chloride usually are prepared in the laboratory, is $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$. When the hydrate is heated, hydrolysis occurs and HCl is liberated. When the material is heated to dryness, only the oxide remains. In solution, the salt is also strongly hydrolyzed. It is used as a mordant, as a reagent in chemical analysis, and in medicine. "Tincture of iron" is a solution of ferric chloride in an alcohol-water mixture. It is used in medicine as a tonic and in the treatment of anemia. It is also used to coagulate the blood in cases of severe bleeding.

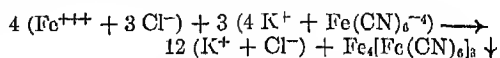
18. Ferric Sulfate, $\text{Fe}_2(\text{SO}_4)_3$

This salt is produced by oxidizing ferrous sulfate. Since it does not crystallize satisfactorily from solutions, it is usually converted into alums, such as ferric ammonium alum, $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ or iron alum, $\text{KFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$. These are readily separated from solutions as well-formed crystals.

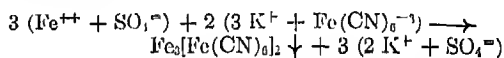
They are used as oxidizing agents in a few reactions in analytical chemistry.

19. Complex Iron Cyanides

The preparation and properties of the ferrocyanides and ferricyanides were discussed in the chapter which dealt with the compounds of nitrogen. Our interest in these substances at present is in their use in tests for ferrous and ferric ions. Ferrocyanide ion reacts with ferric ion to form a dark blue precipitate called *Prussian blue*. This substance is *ferric ferrocyanide*.



Ferricyanide reacts with ferrous ion to form the dark blue insoluble compound called *Turnbull's blue*. This substance is *ferrous ferricyanide*.



Ferrous ferrocyanide, if pure, is white, and ferric ferricyanide is a soluble green compound. Since ferrous ion does not form a blue precipitate with ferrocyanide, the two valence-states of iron can be detected by means of the two reactions shown in these equations. Ferric ions are also detected by means of potassium thiocyanate, KSCN , with which it forms the blood-red, soluble compound, $\text{K}_3^+\text{Fe}(\text{SCN})_6^{3-}$.

Prussian blue is used as bluing and as a pigment in paints.

20 Blue Prints

The paper which is used in making blue prints is made sensitive to light by dipping it in a solution containing ferric ammonium citrate and potassium ferricyanide. The paper is then dried in the dark. It is covered with a mixture of the two salts and ferric ferricyanide, which gives it a green color. A sheet of this paper is covered with tracing cloth, upon which the design to be blue-printed has been drawn, and exposed to the light. The ferric compound is reduced to the

ferrous state, wherever light passes through the tracing cloth and strikes the paper. There is no change beneath the lines in the drawing. The paper is developed by being dipped in water. This brings about a reaction between ferrous and ferricyanide ions, forming insoluble Turnbull's blue wherever the ferrous salt has been made. At other points, where there has been no reduction, the unchanged substances are completely removed by dissolving in the water. The blue print, therefore, is like a photographic negative in that white regions on the paper correspond to black portions of the original

COBALT

21. History and Occurrence

The name of this element is derived from the German word *kobold*, which means "a goblin." For a long time, the minerals from which cobalt was finally prepared resisted all efforts to decompose them, and it was thought that goblins and devils carefully guarded the minerals and thwarted man's attempts to liberate the metal. Brandt succeeded in preparing the element in 1735. Cobalt occurs in nature in many minerals that contain compounds of iron, nickel, silver, arsenic, and copper. The common cobalt minerals are compounds of the element with sulfur or arsenic: *cobaltite*, CoAsS , *smallite*, CoAs_2 , and *linnaitite*, Co_3S_4 . The richest deposits of these minerals are in Ontario, Canada. The ores of this region contain large amounts of silver, and cobalt is produced as a by-product of the silver smelters. Cobalt is also produced from ores mined in the Belgian Congo, and large, undeveloped deposits are located elsewhere in Africa.

22 Metallurgy

The cobalt ores of Ontario are smelted in a small blast furnace, from which the silver is recovered as bullion, and the other metals are collected as a complex mixture of arsenides and sulfides. The latter is roasted with

suitable fluxes to remove arsenic and iron. Heating it with sodium chloride converts the cobalt and nickel into chlorides, which are extracted with water. The nickel and cobalt are then precipitated as $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$. The separation of these two metals is extremely difficult. In the Mond process the oxides are reduced with water gas, and nickel is removed by forming the volatile carbonyl, $\text{Ni}(\text{CO})_4$, in an atmosphere of carbon monoxide. Metallic cobalt is made by the Goldschmidt process or by the reduction of the oxide with carbon.

23. Properties and Uses

Pure cobalt is silvery-gray, malleable, ductile, and magnetic at ordinary temperatures. It melts at 1480° . Like iron, it displays the phenomenon of passivity. It is less readily oxidized than iron. It reacts with oxygen to form Co_3O_4 , which is analogous to Fe_3O_4 . When it is heated to redness, it slowly displaces hydrogen from steam, and at ordinary temperatures it reacts slowly with non-oxidizing acids. It also combines directly, at different temperatures, with the halogens, carbon, and sulfur.

Cobalt is not widely used. Its use in making *carbaloys* has been mentioned in the discussion of tungsten (page 727). Its most important use is in the manufacture of *stellite*, an alloy containing iron, cobalt, and varying percentages of metals such as chromium, nickel, tungsten, and molybdenum. Stellite is used in making high-speed cutting tools, surgical instruments, etc. A coat of stellite is sometimes placed on iron and steel to form a hard surface that resists abrasion. The coating of metals with stellite is called *stelliteing*.

24 Compounds of Cobalt

The oxides of cobalt are CoO , Co_2O_3 , CoO_2 , and Co_3O_4 . The last of these is a compound, $\text{CoO} \cdot \text{Co}_2\text{O}_3$, or $2 \text{CoO} \cdot \text{CoO}_2$. The monoxide is used to produce a blue color in glass, enamels, and glazes, and in painting blue designs on china. In all of these cases,

the blue color is due to the formation of a cobaltous silicate. Powdered blue cobalt glass is called *small* and is used for similar purposes and as a pigment. The trioxide, Co_2O_3 , is made by heating $\text{Co}(\text{NO}_3)_2$. When the hydroxide, $\text{Co}(\text{OH})_3$, is heated to drive off water, Co_3O_4 instead of Co_2O_3 is formed. The dioxide is made by the action of vigorous oxidizing agents upon cobaltous compounds in alkaline solutions. Although cobalt forms cobaltites, in which it acts as a non-metal, the principal compounds of the element are salts in which cobalt acts as a metal. The cobaltic salts are unstable and are not well known. The cobaltous salts, such as CoSO_4 and CoCl_2 , are easily prepared and are the most important compounds of the element. The anhydrous salts are blue and the hydrates are red. Cobalt forms many complex salts in which its valence is 2 or 3. Examples of these complexes are $\text{Na}_4\text{Co}(\text{CN})_6$, $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, and $\text{K}_3\text{Co}(\text{NO}_2)_6$. Potassium cobalti-nitrite, $\text{K}_3\text{Co}(\text{NO}_2)_6$, dissolves only slightly. This complex salt is formed whenever a cobaltous salt, a potassium salt, and a nitrite are brought together in a solution containing acetic acid. This reaction is used as a test for both potassium and cobaltous ion.

In qualitative analysis, cobalt is precipitated as the sulfide in the group with iron, zinc, manganese, and nickel. The sulfides of nickel and cobalt do not precipitate in moderately acid solutions, but when they are once formed they are dissolved by acids only slowly. Advantage is taken of this behavior in separating cobalt and nickel from iron and other metals. Cobalt may then be detected by precipitating it as $\text{K}_3\text{Co}(\text{NO}_2)_6$, since nickel forms no precipitate under the conditions that are used in forming this compound.

NICKEL

Nickel ores, like those of cobalt, are difficult to reduce; consequently, early efforts to produce the metal which they contain were

unsuccessful. It was thought that these minerals contained copper and so they were called *kupfernickel*, a German word from which the element nickel derives its name. *Kupfer* refers to copper, and *nickel* to the devil which was thought to prevent the preparation of copper from the mineral. The element was first prepared in 1857 by Cronstedt.

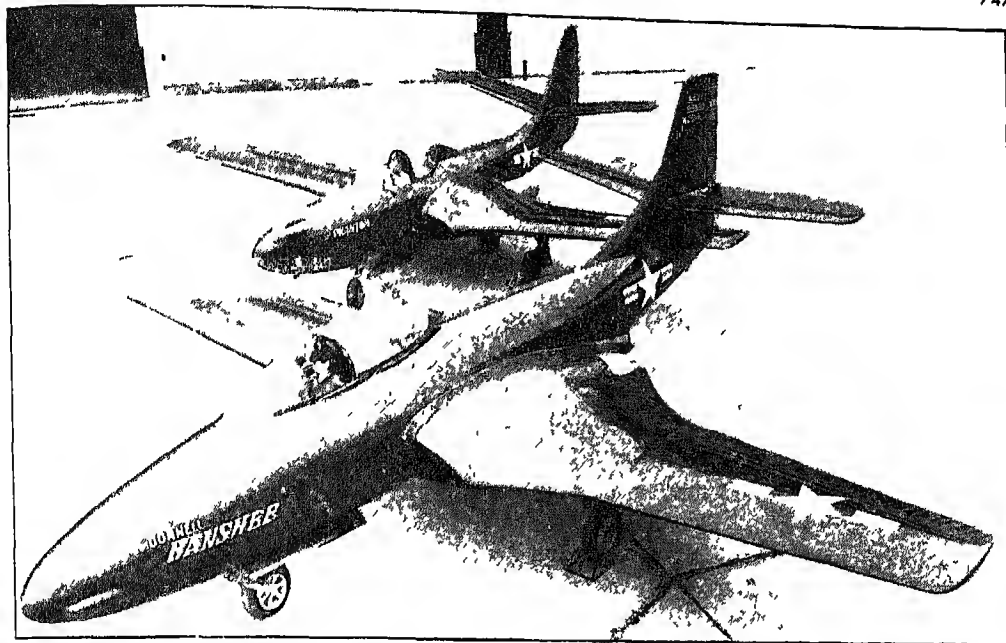
Nickel occurs in meteorites as an alloy with iron, in *garnierite*, $\text{NiO} \cdot \text{MgO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$; and in other minerals in which it is associated with cobalt, copper, iron, and silver as complex sulfides and arsenides. The largest part of the world's supply of nickel is obtained at present from deposits in Ontario, Canada, which contain a mineral composed of the sulfides of iron, nickel, and copper. Some nickel is recovered in the electrolytic refining of copper.

25 Metallurgy

The Canadian ores are roasted and smelted in a blast furnace. This yields a matte of the sulfides of nickel and other metals. The matte is then mixed with silica and treated in a Bessemer converter, in which iron is oxidized and converted into slag. The enriched nickel matte is then further heated and the nickel sulfide is oxidized to the oxide. In another process the matte is heated with sodium sulfide, which dissolves the sulfide of copper and leaves the sulfide of nickel. The residue containing the nickel is then thoroughly roasted to form the oxide, which is reduced by means of carbon. Still another method is the Mond process, which has been described in the section dealing with cobalt. The nickel carbonyl, which is formed in this process, is decomposed, when it is heated, into pure nickel.

26 Properties and Uses

Nickel is a silvery, hard metal, which takes a high polish. It is malleable and can be welded with iron. Like iron and cobalt, it is highly magnetic. It melts at 1452° . It is not attacked by air under ordinary condi-



Courtesy of The International Nickel Company, Inc.

Figure 327 Nickel Alloys Used in Jet Plane Engines Resist the Destructive Effect of High Temperatures

tions, but very finely divided nickel ignites spontaneously. In its action upon steam and dilute acids, it resembles cobalt very closely, although it is less reactive towards all of these. It dissolves readily in dilute nitric, but is made passive by the concentrated acid. It is not attacked by fused alkali, and for this reason crucibles made of nickel are used in the laboratory when such fusions have to be made.

Nickel is used in making several varieties of alloy steels and many other alloys. *Monel* metal, which contains essentially nickel and copper with small percentages of iron, is one of the most important nickel alloys with non-ferrous metals. This alloy is familiar as a covering for kitchen sinks and soda fountains, but it is more widely used for blades of propellers and turbines, steam lines, valves, and many forms of hardware. *German silver* is an alloy of copper, nickel, and zinc. The alloy used for nickel coinage (U.S.) contains 25 per cent of nickel and 75 per cent of copper. *Constantan* (Ni 40, Cu 60) is used in

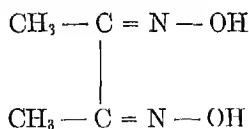
making thermocouples. *Manganin* (Ni 4, Cu 84, Mn 12) is used as electrical resistance in heating devices in the same way that *nichrome* (page 722) is used. *Invar* is a high-nickel steel (Ni, 36). There are several hundred such alloys, each specifically adapted to some purpose. *Platinite*, containing iron and about 44 per cent of nickel, is used in electric light bulbs, and wherever metal must be sealed in glass as lead-in wires.

Nickel is also used extensively to electroplate iron, copper, and other metals. The nickel coating is attractive because it can be highly polished, and it is resistant to corrosion. Chromium plating has replaced nickel plating to a considerable extent, but has not reduced the use of nickel materially in this respect, since an article which is to be chromium plated is usually plated first with nickel. An active, finely divided nickel powder is produced by reducing the oxide with hydrogen below 300°. This material is used as a catalyst in the hydrogenation of fats (page 588) and in the separation of

hydrogen from the carbon monoxide in water gas (page 111)

27. Compounds of Nickel

Nickel has a valence of positive 2 in almost all of its compounds. It forms the monoxide, NiO , when it is heated in air. This oxide and the hydroxide, Ni(OH)_2 , are basic. The trioxide, Ni_2O_3 , is produced by the action of strong oxidizing agents upon nickel salts in an alkaline solution. The Edison storage battery uses electrodes of iron and nickel trioxide with a bath of sodium hydroxide instead of lead, lead dioxide, and sulfuric acid, the active substances in the ordinary "lead" storage battery. Nickel also forms the oxides Ni_2O_3 and Ni_3O_4 . The dioxide has feeble acidic properties and forms compounds called nickelites, when fused with the carbonates of certain metals. The nickelous salts are usually green or blue in color. The most familiar of these are $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, and nickel ammonium sulfate, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. The last of these is used in the solution from which nickel is plated. Nickel combines with carbon monoxide at 50° or lower to form nickel carbonyl, Ni(CO)_4 . Like iron and cobalt, it forms many complex compounds. Nickel sulfide resembles cobalt sulfide in behavior. The most widely used reagent for the detection of nickelous ion, Ni^{++} , is a solution of dimethylglyoxime,



Nickel replaces the two hydrogen atoms of the hydroxyl groups of this substance and forms a red precipitate of a nickel salt of dimethylglyoxime

THE PLATINUM FAMILY

Ruthenium, rhodium, palladium, osmium, iridium, and platinum are known as the *platinum metals*, since they have very similar properties and are found naturally together

Although there are some likenesses between these metals and iron, cobalt, and nickel, the difference in activity is very pronounced, the platinum metals being the most noble of the metals.

28. Occurrence and Metallurgy

These metals occur usually in the free state. Platinum is found as nuggets or small grains in alluvial sands. It is not pure but is alloyed with the other platinum metals, with gold, and with other metals. Platinum is found in the combined state in one mineral, the arsenide, *sperrylite*, PtAs_2 . The most important deposits of platinum are in the Ural Mountains of Russia, in Colombia, and in South Africa. Minor deposits occur in some of the western parts of the United States. Canada produces platinum as a by-product of the smelting of the nickel ores of Ontario, and some is produced during the electrolytic refining of copper, nickel, and gold. The source of the other members of the family is crude, native platinum, with which they are alloyed.

To separate platinum from the other metals with which it occurs, the native ore is first washed in running water in sluices, or it is panned to remove the sand and other materials in which the platinum particles are found. The metal is then treated with aqua regia which dissolves the platinum, forming chloroplatinic acid, H_2PtCl_6 . Some of the other metals also dissolve but osmium and iridium, which are usually present in larger amounts than the others, are left as an undissolved alloy. The platinum is then precipitated as ammonium chloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$, by adding ammonium chloride. When this precipitate is heated, it decomposes, and the platinum is set free. When made in this way the metal is spongy and lacks its usual brilliant luster. The massive, compact metal is made by melting the spongy material in an electric furnace.

29. Platinum, Properties and Uses

Platinum is a white metal. Its density is

very high (21.45 g per cc), and its melting point is 1755° . It is somewhat harder than gold, but it can be drawn readily into wire or hammered into sheets. In its finely divided state it adsorbs gases readily. Its catalytic effect upon reactions, such as the combination of hydrogen and oxygen, is undoubtedly due to this property. Its use as a catalyst in the production of sulfuric acid by the contact process and in the oxidation of ammonia by the Ostwald process will be recalled from earlier chapters. The red-hot metal is not attacked by oxygen, and it does not dissolve in the simple acids, not even in hot nitric acid. Free chlorine reacts with it to form platinum tetrachloride, PtCl_4 . It dissolves in aqua regia, forming chloroplatinic acid, H_2PtCl_6 . When heated with fused alkali hydroxides or nitrates, it is converted into platmates, such as Na_2PtO_3 . Because of its resistance to the effects of an acid and most reagents, and because of its high melting point, platinum is used in the manufacture of crucibles, wire, and foil for many laboratory purposes. These must be used, of course, with due regard for the effect of fused alkalis, free chlorine, and metals, many of which alloy with platinum. At elevated temperatures the metal combines with phosphorus, sulfur, carbon, and silicon. Mixtures in which metals or these four non-metals may be liberated by reduction should never be heated in platinum crucibles.

Platinum is used in dentistry and in the manufacture of jewelry, X-ray tubes, crucibles and dishes for laboratory use, and electrical apparatus. It is also useful as a catalyst in many reactions. Since the metal has the same coefficient of expansion as glass, it is used wherever metal must be sealed in glass, as, for example, in making the electrodes in electric lamps, X-ray tubes, neon signs, and electrical discharge tubes of all kinds. Certain alloys have replaced it in some forms of scientific apparatus, tantalum is also used for similar purposes. An alloy of gold and palladium is used as a substitute for platinum in crucibles. A small sheet of platinum

covered with finely divided *platinum black* and saturated with hydrogen is used as the hydrogen electrode in electrical cells. The use of finely divided platinum or fine wire in gas lighters depends upon the ability of the metal to adsorb oxygen and hydrogen or other combustible gases.

30 Compounds of Platinum

The valence of platinum is always positive and may be 1, 2, 3, 4, or 6. The only important compounds of the metal are those in which its valence is 2 or 4. It forms an extremely large number of complex compounds. The tendency to form platmates when heated with a mixture of an alkali hydroxide and the nitrates of an alkali metal, or with other strong oxidizing agents, indicates a slight acid-forming property. It forms two chlorides, PtCl_2 and PtCl_4 . Both of these react with an excess of HCl to form complex acids, PtCl_2 forming *chloroplatinous acid* and PtCl_4 forming *chloroplatinic acid*. Each of these acids forms a series of salts, e.g. K_2PtCl_4 and K_2PtCl_6 . The chloroplatmates are the most important compounds of the metal.

31 Ruthenium

Ruthenium is a gray, hard, brittle metal. The valence of the metal in its compounds may be positive 2, 3, 4, 6, 7, or 8. In its higher valence states the element acts in much the same manner as hexavalent and heptavalent manganese, forming ruthenates, Na_2RuO_4 , and per ruthenates, NaRuO_4 . The tetroxide, RuO_4 , appears to be neither basic nor acidic. In its lower valences (2 and 3) ruthenium forms metallic salts, such as RuCl_2 and RuCl_3 . The dioxide, RuO_2 , is amphoteric.

32. Osmium

Osmium is the heaviest of the metals (density 22.48), and is hard enough to scratch glass. It forms *osmates* (K_2OsO_4), chlorides and fluorides (OsCl_2 , OsCl_4 , OsF_3 , and OsCl_3), oxides OsO , Os_2O_3 , OsO_2 , and OsO_4 , and

many complex compounds. The tetroxide, OsO_4 , in which osmium apparently has a valence of 8, is volatile. It is sometimes called *osmic acid*, although it does not act as an acid. It is a very active oxidizing agent and is used to harden and stain biological materials. The octafluoride and octachloride are also volatile and resemble true salts very little. Osmium tetroxide reacts with an excess of the chloride ion to form the complex ion, OsCl_6^{2-} . This ion is found in the chlorosmates, e.g. K_2OsCl_6 , which are analogous to the chloroplatmates.

33. Rhodium

This metal is softer than osmium or ruthenium and melts at a lower temperature. It looks like aluminum, but of course is much more noble. In its principal compounds the element has a valence of 2 or 4. Chlorine attacks the metal more readily than it does platinum, forming the trichloride, RhCl_3 . Like the other metals of the family, rhodium forms many complex compounds.

34. Iridium

This metal is silvery-white and is somewhat softer than osmium. It is sometimes used, in the form of an alloy with platinum or gold, to make crucibles and other laboratory articles, which are usually made of pure platinum. Pen points are tipped with a very hard alloy of iridium and osmium, called *iridosmine*. Iridium is the most expensive of the platinum metals. In its compounds iridium has a valence of 3 or 4. It forms the following representative compounds: IrCl_3 ; Ir_2O_3 , K_3IrCl_6 , IrO_2 , K_2IrCl_6 ; and Na_2IrO_4 .

35. Palladium

This metal closely resembles platinum. It is soft and malleable and melts at a lower temperature than any other member of the family. It has a pronounced tendency to adsorb many gases, especially hydrogen (page 112). The most abundant and least expensive of the six metals of the family, it is used in dentistry, in the manufacture of

scientific instruments and jewelry, and as a catalyst. In its compounds palladium has a valence of 2 or 4. It is more strongly basic than the others; it dissolves in boiling nitric acid to form $\text{Pd}(\text{NO}_3)_2$, while the others are insoluble. Other typical compounds are K_2PdCl_4 , K_2PdCl_6 , PdO , and PdO_2 .

Review Exercises

1. What are the principal ores of iron? In what other forms does the element occur in nature?
2. Write the equations for the reactions that occur in the blast furnace and indicate the portion of the furnace where each reaction occurs.
3. What is the advantage of height in the blast furnace? Why should the furnace be operated as nearly continuously as possible?
4. What are the products of the blast furnace?
5. Compare the properties and composition of pig iron, wrought iron, and steel.
6. Explain the furnaces used and the reactions involved in the two principal processes for making steel. What are the relative advantages and disadvantages of each of these?
7. What changes occur in the heat treatment of steels? What is case-hardened steel?
8. Identify Venetian red, dun iron, green vitriol, crucible steel, malleable cast iron, stellite, Prussian blue, cementite, manganite.
9. Why is aluminum sometimes used in the manufacture of steel? What other substances are used for the same purpose?
10. How would you determine whether or not there was any ferrous sulfate in a sample of ferric sulfate?
11. Summarize the properties of nickel and cobalt, comparing them with those of iron. Which of these elements resembles iron more closely? State one or two facts to support your answer.
12. What are the sources of nickel and cobalt? How are they used?
13. What are the sources of the metals of the platinum family? How do these elements differ from iron, cobalt, and nickel?
14. Name three chemical properties of platinum. Name two or three of its most important compounds.

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APPENDIX

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APPENDIX

TABLE I
Vapor Pressure of Water at Different Temperatures

Temperature (degrees C)	Vapor Pressure (mm. of mercury)	Temperature (degrees C.)	Vapor Pressure (mm. of mercury)	Temperature (degrees C)	Vapor Pressure (mm. of mercury)
0	4.58	22	19.83	40	55.32
5	6.54	23	21.07	45	71.88
10	9.21	24	22.38	50	92.51
11	9.84	25	23.76	55	118.04
12	10.52	26	25.21	60	149.38
13	11.23	27	26.74	65	187.54
14	11.99	28	28.35	70	233.70
15	12.79	29	30.04	75	289.10
16	13.63	30	31.82	80	355.10
17	14.53	31	33.70	85	433.60
18	15.48	32	35.66	90	525.76
19	16.48	33	37.73	95	633.90
20	17.54	34	39.90	100	760
21	18.65	35	42.18		

TABLE II
Solubility Products*

Compound	Solubility (Product)	Compound	Solubility (Product)
Aluminum hydroxide, $\text{Al}(\text{OH})_3$	1×10^{-15}	Ferrous sulfide, FeS	4×10^{-20}
Arsenic trisulfide, As_2S_3	4×10^{-29}	Lead chloride, PbCl_2	1×10^{-4}
Antimony trisulfide, Sb_2S_3	3×10^{-27}	Lead chromate, PbCrO_4	2×10^{-11}
Barium carbonate, BaCO_3	8×10^{-6}	Lead sulfate, PbSO_4	1×10^{-8}
Barium chromate, BaCrO_4	2×10^{-10}	Lead sulfide, PbS	3×10^{-28}
Barium oxalate, BaC_2O_4	2×10^{-7}	Magnesium hydroxide, $\text{Mg}(\text{OH})_2$	1×10^{-11}
Barium sulfate, BaSO_4	1×10^{-10}	Manganese sulfide, MnS	2×10^{-15}
Bismuth sulfide, Bi_2S_3	5×10^{-33}	Mercuric sulfide, HgS	4×10^{-55}
Cadmium sulfide, CdS	4×10^{-29}	Nickel sulfide, NiS	2×10^{-24}
Calcium carbonate, CaCO_3	1×10^{-8}	Silver chloride, AgCl	1×10^{-10}
Calcium chromate, CaCrO_4	2×10^{-2}	Silver sulfide, Ag_2S	2×10^{-48}
Calcium oxalate, CaC_2O_4	2×10^{-9}	Strontium carbonate, SrCO_3	1×10^{-9}
Calcium sulfate, CaSO_4	6×10^{-5}	Strontium chromate, SrCrO_4	3×10^{-5}
Cobalt sulfide, CoS	3×10^{-26}	Strontium oxalate, SrC_2O_4	6×10^{-8}
Cupric sulfide, CuS	9×10^{-15}	Strontium sulfate, SrSO_4	3×10^{-7}
Ferric hydroxide, $\text{Fe}(\text{OH})_3$	1×10^{-36}	Zinc sulfide, ZnS	1×10^{-23}

* The principle of the solubility product can be applied only to the saturated solutions of slightly soluble substances. For such substances, the value of the solubility product can be calculated from the solubility expressed as gram-molecular weights per liter. Since the saturated solutions of slightly soluble substances are very dilute, we may assume that they are completely ionized, the Debye-Huckel theory, of course, regards them as actually 100 per cent ionized. The solubility products in this table have been calculated for 18°-20°.

FOUR-PLACE LOGARITHMS OF NUMBERS

N	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
1	0000	043	086	128	170	212	253	294	334	374	4	8	12	17	21	25			
2	414	458	492	531	569	607	645	682	719	755	4	8	11	15	19	23			
3	792	828	864	899	934	969	1004	1038	1072	1106	3	7	10	14	17	21			
4	1139	1178	1216	1253	1289	1325	1360	1395	1430	1464	3	6	10	13	16	19			
5	1516	1556	1595	1633	1670	1706	1742	1778	1813	1848	3	5	9	12	15	18			
6	1961	2002	2042	2081	2119	2156	2192	2228	2264	2300	3	4	8	11	14	17			
7	2404	2444	2483	2521	2558	2594	2630	2666	2701	2736	3	3	7	10	13	16			
8	2779	2818	2856	2893	2929	2965	3000	3035	3070	3105	3	2	6	9	12	15			
9	3160	3198	3235	3271	3307	3342	3377	3412	3446	3481	3	1	5	8	11	14			
10	3526	3562	3597	3632	3666	3700	3734	3768	3801	3835	3	0	4	7	10	13			
11	3869	3902	3935	3967	3999	4031	4062	4093	4124	4155	3	0	3	6	9	12			
12	4186	4217	4247	4277	4307	4336	4365	4394	4423	4451	3	0	2	5	8	11			
13	4480	4508	4536	4564	4591	4618	4645	4672	4698	4725	3	0	1	4	7	10			
14	4752	4778	4804	4829	4854	4879	4903	4927	4951	4975	3	0	0	3	6	9			
15	4998	5021	5044	5066	5088	5109	5130	5151	5171	5191	3	0	0	2	5	8			
16	5211	5231	5251	5270	5289	5308	5326	5345	5363	5381	3	0	0	1	4	7			
17	5399	5417	5435	5453	5471	5488	5506	5523	5540	5557	3	0	0	0	3	6			
18	5574	5591	5607	5624	5640	5656	5672	5688	5704	5720	3	0	0	0	2	5			
19	5736	5752	5768	5783	5798	5813	5828	5843	5857	5872	3	0	0	0	1	4			
20	5886	5900	5914	5928	5942	5956	5969	5983	5996	6009	3	0	0	0	0	3			
21	6021	6034	6047	6060	6073	6085	6097	6109	6121	6133	3	0	0	0	0	2			
22	6145	6157	6169	6181	6192	6204	6215	6226	6237	6248	3	0	0	0	0	1			
23	6259	6270	6281	6291	6302	6312	6322	6332	6342	6352	3	0	0	0	0	0			
24	6362	6371	6381	6390	6400	6409	6418	6427	6436	6445	3	0	0	0	0	0			
25	6454	6463	6472	6481	6490	6499	6508	6517	6525	6534	3	0	0	0	0	0			
26	6543	6551	6559	6567	6575	6583	6591	6599	6607	6615	3	0	0	0	0	0			
27	6624	6631	6638	6645	6652	6659	6666	6673	6680	6687	3	0	0	0	0	0			
28	6694	6701	6708	6714	6721	6728	6734	6740	6746	6752	3	0	0	0	0	0			
29	6758	6764	6770	6776	6782	6788	6793	6799	6804	6809	3	0	0	0	0	0			
30	6814	6819	6824	6829	6834	6839	6844	6849	6854	6859	3	0	0	0	0	0			
31	6863	6868	6873	6878	6883	6888	6893	6898	6903	6908	3	0	0	0	0	0			
32	6913	6918	6923	6928	6933	6938	6943	6948	6953	6958	3	0	0	0	0	0			
33	6963	6968	6973	6978	6983	6988	6993	6998	7003	7008	3	0	0	0	0	0			
34	7013	7018	7023	7028	7033	7038	7043	7048	7053	7058	3	0	0	0	0	0			
35	7063	7068	7073	7078	7083	7088	7093	7098	7103	7108	3	0	0	0	0	0			
36	7113	7118	7123	7128	7133	7138	7143	7148	7153	7158	3	0	0	0	0	0			
37	7163	7168	7173	7178	7183	7188	7193	7198	7203	7208	3	0	0	0	0	0			
38	7213	7218	7223	7228	7233	7238	7243	7248	7253	7258	3	0	0	0	0	0			
39	7263	7268	7273	7278	7283	7288	7293	7298	7303	7308	3	0	0	0	0	0			
40	7313	7318	7323	7328	7333	7338	7343	7348	7353	7358	3	0	0	0	0	0			
41	7363	7368	7373	7378	7383	7388	7393	7398	7403	7408	3	0	0	0	0	0			
42	7413	7418	7423	7428	7433	7438	7443	7448	7453	7458	3	0	0	0	0	0			
43	7463	7468	7473	7478	7483	7488	7493	7498	7503	7508	3	0	0	0	0	0			
44	7513	7518	7523	7528	7533	7538	7543	7548	7553	7558	3	0	0	0	0	0			
45	7563	7568	7573	7578	7583	7588	7593	7598	7603	7608	3	0	0	0	0	0			
46	7613	7618	7623	7628	7633	7638	7643	7648	7653	7658	3	0	0	0	0	0			
47	7663	7668	7673	7678	7683	7688	7693	7698	7703	7708	3	0	0	0	0	0			
48	7713	7718	7723	7728	7733	7738	7743	7748	7753	7758	3	0	0	0	0	0			
49	7763	7768	7773	7778	7783	7788	7793	7798	7803	7808	3	0	0	0	0	0			
50	7813	7818	7823	7828	7833	7838	7843	7848	7853	7858	3	0	0	0	0	0			
51	7863	7868	7873	7878	7883	7888	7893	7898	7903	7908	3	0	0	0	0	0			
52	7913	7918	7923	7928	7933	7938	7943	7948	7953	7958	3	0	0	0	0	0			
53	7963	7968	7973	7978	7983	7988	7993	7998	8003	8008	3	0	0	0	0	0			
54	8013	8018	8023	8028	8033	8038	8043	8048	8053	8058	3	0	0	0	0	0			
55	8063	8068	8073	8078	8083	8088	8093	8098	8103	8108	3	0	0	0	0	0			
56	8113	8118	8123	8128	8133	8138	8143	8148	8153	8158	3	0	0	0	0	0			
57	8163	8168	8173	8178	8183	8188	8193	8198	8203	8208	3	0	0	0	0	0			
58	8213	8218	8223	8228	8233	8238	8243	8248	8253	8258	3	0	0	0	0	0			
59	8263	8268	8273	8278	8283	8288	8293	8298	8303	8308	3	0	0	0	0	0			
60	8313	8318	8323	8328	8333	8338	8343	8348	8353	8358	3	0	0	0	0	0			
61	8363	8368	8373	8378	8383	8388	8393	8398	8403	8408	3	0	0	0	0	0			
62	8413	8418	8423	8428	8433	8438	8443	8448	8453	8458	3	0	0	0	0	0			
63	8463	8468	8473	8478	8483	8488	8493	8498	8503	8508	3	0	0	0	0	0			
64	8513	8518	8523	8528	8533	8538	8543	8548	8553	8558	3	0	0	0	0	0			
65	8563	8568	8573	8578	8583	8588	8593	8598	8603	8608	3	0	0	0	0	0			
66	8613	8618	8623	8628	8633	8638	8643	8648	8653	8658	3	0	0	0	0	0			
67	8663	8668	8673	8678	8683	8688	8693	8698	8703	8708	3	0	0	0	0	0			
68	8713	8718	8723	8728	8733	8738	8743	8748	8753	8758	3	0	0	0	0	0			
69	8763	8768	8773	8778	8783	8788	8793	8798	8803	8808	3	0	0	0	0	0			
70	8813	8818	8823	8828	8833	8838	8843	8848	8853	8858	3	0	0	0	0	0			
71	8863	8868	8873	8878	8883	8888	8893	8898	8903	8908	3	0	0	0	0	0			
72	8913	8918	8923	8928	8933	8938	8943	8948	8953	8958	3	0	0	0	0	0			
73	8963	8968	8973	8978	8983	8988	8993	8998	9003	9008	3	0	0	0	0	0			
74	9013	9018	9023	9028	9033	9038	9043	9048	9053	9058	3	0	0	0	0	0			
75	9063	9068	9073	9078	9083	9088	9093	9098	9103	9108	3	0	0	0	0	0			
76	9113	9118	9123	9128	9133	9138	9143	9148	9153	9158	3	0	0	0	0	0			
77	9163	9168	9173	9178	9183	9188	9193	9198	9203	9208	3	0	0	0	0	0			
78	9213	9218	9223	9228	9233	9238	9243	9248	9253	9258	3	0	0	0	0	0			
79	9263	9268	9273	9278	9283	9288	9293	9298	9303	9308	3	0	0	0	0	0			
80	9313	9318	9323	9328	9333	9338	9343	9348	9353										

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